VOL. 1 METALS AND METALLOIDS

VOL. 2 SILICATES

VOL. 3 AUXILIARY MATERIALS

MATERIALS OF HIGH VACUUM TECHNOLOGY

BY

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VOLUME 2

SILICATES

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FOREWORD

THE first volume of the new *Werkstoffkunde der Hochvakuumtechnik* which appeared in 1959, dealt exclusively with metals and metallic conductors. Volume 2 is concerned with a group of insulators of special importance to vacuum technology. If pure oxide ceramics are excepted, the simplest way of referring to this group is "silicate insulators". Glass, fused quartz, ceramics, mica and asbestos are thereby included.

The importance of these materials for tube construction and the extent of practical knowledge about them have increased between the two world wars and thereafter to such an extent that their treatment in the old "ESPE–KNOLL" which was covered in about 57 pages occupies 730 in the present work. This extension was necessary if anything like a thorough presentation was to be given.

In general, the observations made in the foreword to Volume 1 also hold for this volume.

I must thank Mr. J. MRÁČEK for valuable suggestions concerning the chapter "Ceramic Materials of High Vacuum Technology" and also my wife MIROSLAVA ESPE-ZÁMOSTNÁ for active assistance in the collection of material for the manuscript and in proof-reading.

Bratislava, 1959

WERNER ESPE

TRANSLATOR'S ACKNOWLEDGEMENT

THE process of making technical glassware by hand has a vernacular of its own. Grateful acknowledgement is made to Mr. H. L. CROOK, Group Research Manager of United Glass, London, for his help in providing translations of some terms in the German edition of this book which relate to a technology almost obsolete so far as technical glass is concerned.

CHAPTER 10

TECHNICAL GLASSES

[10.1]

10.1. General: Manufacture and Composition

(BÁRTA, DRALLE, [1]GEHLHOFF, KITAIGORODSKIJ, SCHMIDT, SCHOLES, SCHULZ, [1,3]SPÄTE, [1,2]SPRINGER, THIENE, ULLMANN, ZACHARIASEN)

Glass, physically speaking, is a super-cooled fluid which does not form crystals when solidified from the melt since its viscosity rises very rapidly as the temperature falls (amorphous and homogeneous solidification). The molecular aggregates are frozen in and therefore remain in the same state as they were when the material was liquid. In the case of pure quartz glass the same SiO_4 groups exist as those in the crystal itself. However, they do not form an ordered array as in the crystal, but rather an irregular unsymmetrical silicon-oxygen network (Fig. B 10-1). In a sodium-silicate glass, Na^+ ions are present in the meshes of this network (Fig. B 10-2). Thus, a glass has a defined structure but it is not repeated regularly over a region of any size, and the arrangement is therefore not crystalline. For this reason glass is thermodynamically unstable and tends to devitrify, i.e. to form thermodynamically stable crystals if held for long enough at a sufficiently high temperature (the viscosity being correspondingly low), but the temperature must not be so high that the M.P. of the crystal is exceeded.

From the technical standpoint, glass is an inorganic, chemically inert fusion product of oxides, which is hard, brittle (fragile), mostly transparent and practically impermeable to most gases after it has been cooled; it also forms conchoidal fracture-zones.

The starting material for the manufacture of technical glass is generally silicic acid (quartz sand, SiO_2) in which a series of salts are mixed. In the simplest cases the batch consists of 60–75% SiO_2, 5–15% alkali oxide (e.g. Na_2O introduced in the form of soda, Na_2CO_3) and 5–15% alkaline earth oxide (e.g. lime, CaO). Cullet is added to the mixture; to initiate melting it is heated in refractory material by gas-firing.[1] One alternative for this is the use of so-called "pots" of refractory fireclay which will stand temperatures up to 1800°; these are usually arranged several at a time in the furnace. In large-scale production, a refractory-brick tank furnace is used; the starting material is fed in continuously at one end and removal of the molten glass occurs continuously

[1] The main difficulty in melting glasses to exactly prescribed compositions lies in the choice of a suitable material for making the furnace, since almost all furnace brick is more or less soluble in glass in the liquid state. For example, if uptake of Al_2O_3 is to be avoided, quartzware is used for the furnace. In the melting of UV transparent glass, this would be a failure because quartz generally contains traces of TiO_2 which goes into solution and considerably worsens the UV transmission (see Chapter 10.2.XVI). For this reason, sensitive glasses and the above experimental glasses are made in platinum-lined crucibles (see, e.g., [2]TURNER). Pt crucibles are often used for very small experimental melts.

at the other (for further details see, e.g., [3]SPÄTE). By adding to the SiO_2 those materials which were mentioned above, the M.P. is lowered sufficiently for the mix to fuse at 1400–1500°. Heating is maintained for 12–30 hr until the melt is bubble-free ("fining").

TABLE T 10–1. CLASSIFICATION AND CHEMICAL COMPOSITION OF TECHNICAL GLASSES

[10.1]

		CLASS	DESCRIPTION	CHARACTERISTIC CONTENTS [1] (FIGURES ARE w/o)
Soft glasses		I	low alkali lead silicate	SiO_2; *PbO* (40–50); alkali (<10)
		II	alkali lead silicate	SiO_2; *PbO* (20–35); alkali (<10)
		III	alkali lime silicate	SiO_2; *CaO* (5–12); alkali (13–20)
Medium hard glasses		IV	alumo-lime silicate	SiO_2; Al_2O_3 (3.5–10); *CaO* (6–12) alkali (8–23)
		IV*a*	alumo-boro-lime silicate	SiO_2; B_2O_3 (3–8); Al_2O_3 (3.5–10); *CaO* (6–12); alkali (8–23)
		IV*b*	alumo-boro-lime zinc silicate	SiO_2, B_2O_3 (3–8); Al_2O_3 (3.5–10); *CaO* (3–12); *ZnO* (3–7): alkali (8–14)
		IV*c*	alkali borosilicate	SiO_2; B_2O_3 (>10); Al_2O_3 (<6); alkali (5–8)
Hard glasses		V	borosilicate	SiO_2; B_2O_3 (>10); Al_2O_3 (<3)
		VI	alumo-borosilicate	SiO_2; B_2O_3 (5–21); Al_2O_3 (3–20); alkali (<6)
		VII	lead borosilicate	SiO_2; B_2O_3 (15–17); *PbO* (*ca.* 6)
Special glasses	Opal glass	VIII	fluoro-lime zinc silicate	SiO_2; F_2 *ca.* 7; CaO; ZnO
	—	IX	borate	B_2O_3; various oxides
		X	alumoborate	B_2O_3; Al_2O_3; various oxides ($SiO_2 < B_2O_3$)
	UV glasses	XI	phosphate	P_2O_5
		XII	alumophosphate	P_2O_5; Al_2O_3

[1] Contents of less than 4% SiO_2, 3% Al_2O_3, 3% B_2O_3 or 3% PbO are *not* given.

The chief components of technical glasses, in addition to SiO_2, are the following salts and oxides, which are used partly as minerals (lime, kaolinite, potash feldspar, dolomite, powdered marble), partly as chemicals (alkalies, lead oxide): Na_2O, K_2O, MgO, CaO, BaO, ZnO, PbO, B_2O_3, Al_2O_3, P_2O_5, Sb_2O_3. In addition, a large number of other compounds are frequently added as clouding,[2] decolorizing, or coloring agents; or they may be present as trace impurities in the raw materials. Physical and chemical properties vary considerably with the composition chosen. However, depending on the content of SiO_2, B_2O_3, and P_2O_5, definite types can be distinguished such that simple relations

[2] For example, fluorides, which do not readily dissolve and precipitate easily.

[10.1]

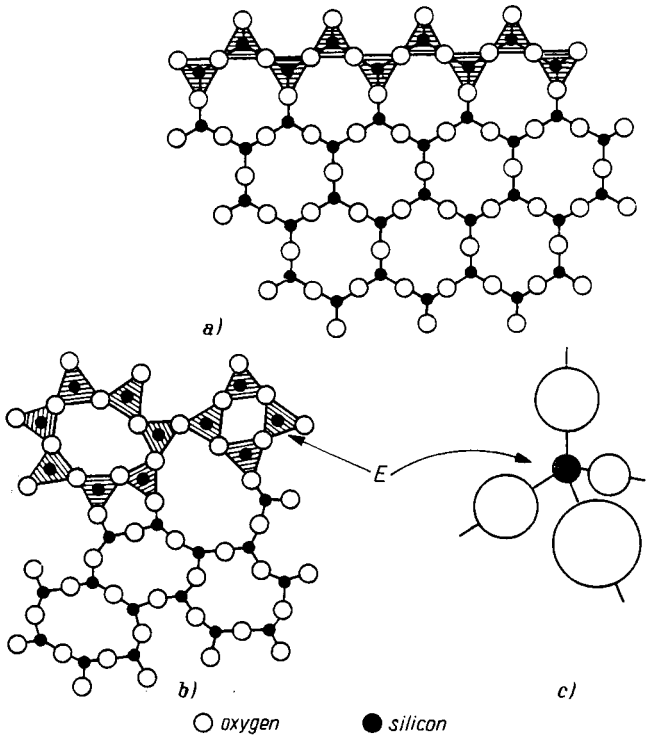


Fig. B 10-1 Schematic representation in one plane of the structure of a quartz *crystal* (*a*) and a quartz *glass* (*b*) produced by melting and rapid chilling (from ZACHARIASEN)

Note: viewed three-dimensionally, each unit of structure consists of Si-atoms with four O-atoms as nearest neighbors (*c*); in the two-dimensional view (*b*), only three O-atoms appear

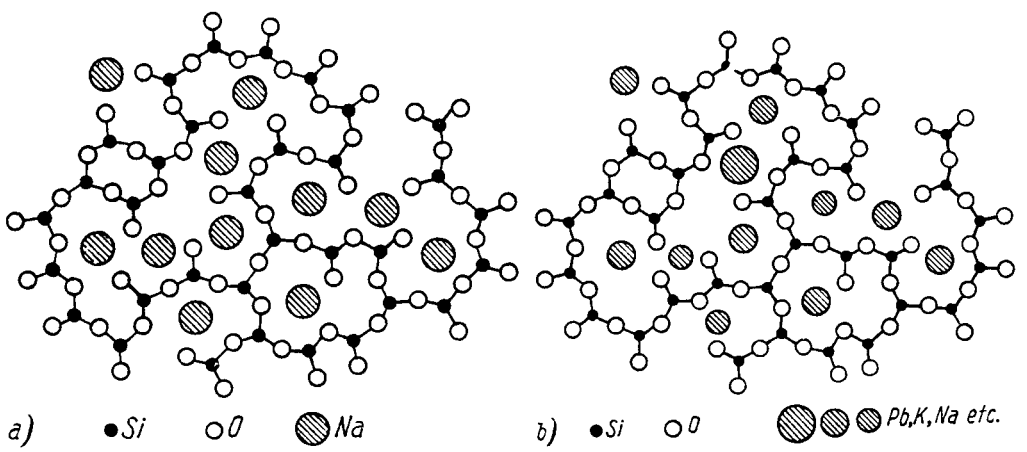


Fig. B 10-2 Schematic representation in one plane of the structure of a binary sodium silicate glass (*a*) and a glass with different lattice modifiers (*b*) (from [1]WARREN)

In the latter case, the hatched circles represent the different diameters of the various metal-oxide ions, which are fused with lattice-forming SiO_2 to make a single glass

hold between the amounts of the individual components and the physico-chemical behavior (see Table T 10–1).

The *devitrification* mentioned above plays a crucial role in the selection of composition.[3] In comparison with the number of possible glass vitrifier combinations, only a few yield good glass, that is one which will tend not to crystallize even when taken slowly through the devitrification range. The next most important parameters which determine composition are *viscosity* as dependent on temperature (affects glass-working processes), the *thermal expansion coefficient*, and the *chemical inertness*. Other pro-
[10.1] perties also are known functions of type and quantity of component: density, specific heat, themal conductivity, and *electrical resistivity*.

The compositions of most technical glasses are found wholly empirically; it is only in the last thirty years, as knowledge of the structural chemistry of glass has increased, that it has been possible to develop [4] types of technical glass which are systems designed with a purpose in view. This is based on the fact that the O-atoms in glass appear as anions and all other components as cations. The latter are divided into "network formers" like Si, which are located in the lattice structure; or they are interstitially situated—surrounded by O-atoms—as "network modifiers". However, there are cations which, according to conditions, may act as either formers or modifiers, so that the following four groups of basic materials for use in glass compositions may be distinguished:

(a) network formers proper or glass-forming materials: Si, B, P;
(b) materials which can be classified as in (a) but which do not form glasses themselves: mainly Al, also Ti, Zr, Be;
(c) amphoterics ("equivocal") materials, which can behave either as formers in the lattice or as modifiers in interstitial positions: Mg, Zn, Pb (the latter will only act as a former when in very high concentrations);
(d) modifiers only: Ca, Ba, Li, Na, K.

By and large, the answer to the important technical question as to what properties are given to the different types of glass by individual cations is as follows:

(a) *Network Formers*

Si: maintains the glassy state in most technical (silicate) glasses, and therefore usually the SiO_2 content is above 50%, except in Na-resistant glass. Increase in SiO_2 content leads to higher stability of the glass, lower expansion coefficient, greater chemical inertness, increased viscosity, and higher M.P.

B: assists the tendency of silicate systems to form glasses, since B_2O_3 itself generally exists in the glassy state, and lessens the chance of devitrification. At high temperatures it considerably reduces viscosity and thus makes the material easier to melt. Reduces thermal expansion, and when in excess of 16% increases the chemical inertness.

P: present in large amounts in glasses designed to resist HF and metal vapors, and which can have no SiO_2 content; in small amounts in Uviol glasses.

[3] See Chapter 10.2.III.

[4] For more details on this see ANNEI, BÁRTA, BESBORODOV, [1,2]DIETZEL, JEVSTROPJEV, JOHNSON, MOREY, [1]SMELT, SOLOMIN, [1]STEVELS, [1]STANWORTH, [1]SUN, [1]VOLF, [1,2]WARREN.

(b) *Network Modifiers Which Do Not Themselves Form Glasses*

Al: markedly increases viscosity and surface tension, and therefore even in small amounts reduces the tendency to devitrify; this improves working with the blowing torch; it is therefore a characteristic component in apparatus glasses. Reduces thermal expansion; raises chemical inertness. Since glasses with high Al content have a short working range which makes working with the blowing torch difficult, the Al_2O_3 content of technical glasses is mostly less than 6%.

Ti, Zr, Be: occur only seldom in technical glasses. [10.1]

(c) *Amphoteric Materials*

Mg: effect not always clear. In small amounts hinders devitrification, in large amounts reduces expansion and mechanical strength and raises viscosity.

Zn: increases chemical inertness, hence is a component of hot-filament lamp glass for tropical use. Reduces expansion. Is said to increase bonding of sealing glasses to metal (effect of adherent oxides as in enamels?), and thus used in SCHOTT Mo-sealing glass 1447^{III}, for example. In large amounts it increases viscosity.

Pb: much increases the T_{*100} point (hence also the electrical resistivity) and very much reduces the viscosity; therefore found in the most widely used foot and sealing glasses for soft-glass tubes, above all for ordinary hot-filament lamps, but blackens due to PbO reduction if the torch flame is not highly oxidizing. PbO raises the density, X-ray absorption and refractive index. Glasses containing PbO show little tendency to devitrify, and have average chemical resistance to H_2O and relatively low resistance to acids.

(d) *Modifiers*

Ca: protects chemical resistance of ordinary soft alkali glasses, but in large amounts leads to devitrification. In large amounts raises viscosity at high temperatures.

Ba: as in the case of B and alkalies, lowers the viscosity markedly, and like Pb, improves electrical insulation properties, for which reason it has recently become a characteristic component of soft glasses for luminous and discharge tubes. Also often used in alkali-resistant (neutral) glasses.

Na: considerably reduces viscosity, and is therefore the most powerful "melting agent"; glasses with high Na content are readily melted. Easily leached out of the glass by H_2O and acids, and when heated, sublimes strongly from the glass surface; much increases the electrical conductivity (glass electrolysis), the dielectric loss ($\tan \delta$), and the thermal expansion (low thermal shock resistance).

K: similar to Na, but has less ionic mobility because of the larger ionic radius, therefore a component of glasses of low dielectric loss in which the amount of K always exceeds that of Na. Because of its radioactivity,[5] should not be used in counting tubes (Geiger–Müller counters).

[5] Ordinary potassium contains, in addition to stable isotopes K^{39} (93.4%) and K^{41} (6.6%), 0.011% radioactive isotope K^{40} which is a beta emitter with a halflife of 4.5×10^9 years decaying to stable Ca^{40}. K-content in glass thus raises the background level of Geiger–Müller counters quite unnecessarily and makes difficulties in the measurement of weak samples and cosmic rays.

The compositions of technical commercial glasses are not always revealed in detail by the manufacturers, as has not been the case for a long time with metallic alloys, where disclosure is usual and useful. This seems incomprehensible since the composition is fairly easily determined analytically. Mostly, the reason behind it is a reluctance to lay down hard and fast tolerances for composition; for experience shows that technical glasses often vary widely in make-up, especially with small-scale manufacturers, in spite of identical designations, and naturally so do the physical properties such as expansion coefficient, transformation temperature and viscosity. It was not until the
[10.1] arrival of machine production of hot-filament lamps and radio tubes that greater precision in composition as well as maintenance of tighter tolerances on dimensions was achieved.

Tables T 10–2 and T 10–2 A give the compositions of a series of commercial glasses of importance to vacuum work.[6] As can be seen, vacuum technology employs almost exclusively alkali silicates ("soft glasses"), alumosilicates ("medium hard"), borosilicates ("hard"), and certain special glasses such as alkali-resistant glass, borate glasses transparent to X-rays, etc.

[6] The compositions (Table T 10–2) and properties (Table T 10–4) of commercial glasses are collected for practical reasons in groups by country of origin and manufacturer (A: America; C: ČSSR; D: Germany; E: England; F: France; H: Holland; J: Japan; Oe: Austria (Österreich); P: Poland; S: USSR; U: Hungary). In each group, glass types are arranged by manufacturer's number. Types without manufacturer's code numbers follow in alphabetical order under the group heading.

TABLE T 10–2. COMPOSITION OF THE MAJOR COMMERCIAL SILICATE GLASSES FOR VACUUM WORK

(Footnotes at the end of the table)

Subdivisions (also valid for table of properties, Table T 10–4)

A	**American glasses**
A 1	CORNING GLASS WORKS
A 2	Various special glasses
A 3	Hard glasses for X-ray tubes
A 4	For TV tubes
A 5	LIBBEY GLASS DIV., OWENS ILLINOIS GLASS CO.
A 6	KIMBLE INDUSTRIAL GLASSES, OWENS ILLINOIS GLASS CO.
C	**Czechoslovakian glasses**
D	**German glasses**
I	Pre-war manufacture and now made in Western Germany (Federal Republic of Germany, FRG)[61]
D 1	ALT, EBERHARD UND JÄGER, Ilmenau[62]
D 2	DEUTSCHE SPIEGELGLAS-GESELLSCHAFT
D 3	GLASWERK G. FISCHER, Ilmenau[62]
D 4	GERRESHEIMER GLASWERKE
D 5	GREINER UND FRIEDRICHS, Stützerbach
D 6	GUNDELACH[62]
D 7	PUTZLER[62], PENZIG o.L.; now PEILL UND PUTZLER, Düren
D 8	OSRAM, Weisswasser[62] and Augsburg
D 9	SCHOTT UND GEN., Jena, Eastern Germany (German Democratic Republic, GDR) and Glaswerk Mainz-FRG (see also D 22)
D 10	SCHÜBEL[62]
D 11	SENDLINGER OPTISCHE GLASWERKE, Berlin-Zehlendorf
D 12	SOPHIENHÜTTE RICHARD BOCK, Ilmenau[62]
D 13	RUHRGLAS, Essen-Karnap
D 14	GLASWERK-WERTHEIM
D 15	Various West German firms
II	Now made in Eastern Germany[61]
D 16	VEB SPEZIALGLASWERK EINHEIT, Weisswasser (cf. D 8)
D 17	VEB GLASWERK FISCHER, Ilmenau (cf. D 3)
D 18	VEB GLASWERK GRENZHAMMER
D 19	VEB GLASWERK HASELBACH
D 20	VEB GLASWERK ILMENAU (cf. D 1)
D 21	VEB GLASWERK SCHMIEDEBERG
D 22	VEB GLASWERK SCHOTT, Jena (cf. also D 9)
D 23	VEB GLASWERK SCHOTT, Gehlberg (cf. also D 6)
D 24	VEB GLASWERK SOPHIENHÜTTE, Ilmenau (cf. D 12)
D 25	VEB GLASWERK STÜTZERBACH (cf. D 5)
E	**English glasses**
E 1	BRITISH THOMSON-HOUSTON (BTH)
E 2	CHANCE BROS. LTD.
E 3	GEN. ELEC. CO., Wembley (GEC)
E 4	See DOUGLAS
E 5	See PARTRIDGE
E 6	PLOWDEN AND THOMPSON LTD., Stourbridge
F	**French glasses**
F 1	CRISTALLERIE DE BACCARAT
F 2	SOC. FRANC. RAD. ELECTR.
F 3	ST. GOBAIN
H	**Dutch glasses**
H 1	PHILIPS GLOEILAMPENFABRIEKEN N. V.
J	**Japanese glasses**
Oe	**Austrian glasses**
Oe 1	MOOSBRUNNER GLASFABRIKEN A.G.
P	**Polish glasses**
S	**Russian glasses**
U	**Hungarian glasses**

[10.1]

TABLE T 10–2. COMPOSITION OF THE MAJOR COMMERCIAL SILICATE GLASSES FOR VACUUM WORK

	TRADE NAME	α [10^{-7}/°C]	CONTENT (w/o) SiO_2	B_2O_3	PbO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	BaO	MgO	OTHER	FOOTNOTE
A	**American glasses**													
A 1	Mfr.: CORNING (for older names see Table T 10–4, suppl. I)													
	G 80 (thermometer glass)		72	10	2	5		10						
	0010 (Soft glass)	91	63		20	0.3		7.3	6	1			Mn_2O_3 : 1	
			63.1		20.2	0.28		7.6	5.5	0.94				(26)
	0080 (lamp bulbs)	92	73.6					17.2		5.4		3.7		(75)
			72			1		17		x		x	CaO + MgO : 10	(85)
	0120 (soda-lime lead)	89	57.0		29.4	1.5		4.1	7.3	0.2		0.2		(75)
	1720 (ignition tube glass)		59.2	4.6		22.2				4.4		9.9		(75)
	3320 (G-371-BN)	41	75	12.7	3.4	2.4		4.6					U_3O_8 : 1.8	(8)
	7050 (clear sealing, G-705-AJ)	46	67	22		2–5		6.5						(26)
			67	22		2		3.5	4.0					(27)
	7052 Kovar glass (like 184, see this Table, A 2)		67	22		2.0		6.5						(75)
	7070 (tan $\delta = 6 \times 10^{-4}$)	32	69.9	25.7		1		1.5	1.4	0.3			Li_2O : 0.2	(47)
			70.55	25.22		1.07	0.03	2.07	0.41	0.07			Li_2O : 0.2; As_2O_3 : 0.38	(46)
	7520 (thermometer glass G-750-AJ)	61	72	10		5		10						
	7720 (Nonex G-702-P)[3]	36	73	16.5	6	—		4.5						
			73	14	5.7	1.7		4.4	—					(8)
			73.2	16.1	6.4	—		4.3	—	—	—	—		(16)
			73.0	16.5	4.0	2.0	(31)	4.5	—	—	—	—		(26)
			70	16.3	6.1	2.1		—	5.1	0.2				(27)
			73.0	16.5	6.0	—	—	4.5						(60)
	7740 (G-726-MX) "Pyrex"[3]	≈ 33	80	13		2		4						(8)
			80.5	12.9		2.2		3.8	0.4	(0.2)				(60) (75)
	7900, 7910, 7911 (Vycor)[3]	8	96.3	2.9		0.4		0.02	0.02					(35) (86)
	9700 (Corex phosphate glass)	37	2.1	4.2				0.6		25.1		0.6	P_2O_5 : 66.5	(75)
	Pyrex[3], see also 7740	32—33	80.7	12		2.2		4.2	—	0.3				(37) (26)
			80.5	11.8		2.0		4.4	0.2	0.3		0.1	As_2O_3 : 0.7	see also (39)
			80.8	12.0		2.3	0.2	4.1	0.1	0.3			As_2O_3 : 0.2	(3)
			80.2	12		3		3.9	0.3	0.2			Sb_2O_3 : 0.3	(3)
	Na-resistant glass, see Table 10–17B		82	12		2.8		4.2						(83)

A 2	*American glasses for special purposes*														
	184 Kovar glass	49	65	23		5		7							(18)
	286 (CrFe sealing)	101	54		29			5	8		4				(18) (24)
			54		29.7			3.8	10.3		1.9				
	"430-Ti" sealing glass for CrFe	100	71.3			2.0 *		17.4			9.0		As_2O_3 : 0.30		(92)
	542x (Fe sealing)[89]	125	46.5		31.46	1.42		6.05	14.08	1.09			Li_2O : 0.5 — 1.0[88]		(1)
	542 (Fe sealing)	113	45		30			6	14	(3)			CaF_2 : 5; (F_2 : 5)		(18) (23) (80) (81)
		≈ 120	45		32			6	12				CaF_2 : 5		(82)
	1075 (FeNi 42 sealing)	51	34	28	29	7		2							(18)
	Low-loss glass, after HOOD ($\tan\delta = 4.2\times10^{-4}$)		70	26.5	—	(48)	—	1.75	1.75	—	—	—	(F)[87]		
	idem, after ARMISTEAD ($\tan\delta = 4.5\times10^{-4}$)		47	—	—	—	—	5.1	12	—	35	—	Li_2O : 0.9		
	Ceramic sealing glass RCA No. 120[76]		13	12	75										(75)
	Insulation glass for lampbases, Vitrit glass		60.6	—	—	6.3		9.2	3.1	5.8		3.9	MnO : 9.7		(75)
			69.0	0.1	—	1.0		16.0	0.8	7.5		1.2	CoO : 0.5		(75)
A 3	*American hard glasses for X-ray tubes* (from BLACK; see also ZUNICK)														
	L 605 (OWENS ILLINOIS GLASS Co.)	49	64.9	22.5		4.9	0.08	7.0					CeO_2 : 0.5; Sb_2O_3 : 0.11		(20) Kovar and Mo glass
	Idem ([3]NORTON)		90			3		7							(85)
A 4	*American glasses for TV tubes*[77]												As_2O_3	Sb_2O_3	NiO	CoO	
	"Neutral" glass, lightly colored — I		55.2			7.5	0.3	10.0	16.1	5.2		3.6	0.4	0.4	0.001	0.003	(75)
	II		57.8			8.0	0.1	22.4	0.9	6.5		3.2	0.7	0.3	0.02	—	
	III		52.4			11.9	0.2	22.8	1.3	6.8		2.7	0.6	—	0.2	—	

	TRADE NAME	MFR.	α [10^{-7} 1/°C] (20—300 °C)	CONTENT (w/o) SiO_2	B_2O_3	PbO	Al_2O_3	Na_2O	K_2O	CaO	BaO	MgO	OTHER	NOTES
C	**Czechoslovakian glasses**[49]													
	AH	Po	89	70.7	2.3		4.2	13.9	1.9	7				Soft apparatus-glass
	C glass	Ka	47—50	55.5	8.8		15.2	0.8		17.5		2.2		Alkali-free, for braid[51]

TABLE T 10–2 *(continued)*

	TRADE NAME	MFR.	α [10^{-7} 1/°C] (20—300 °C)	CONTENT (w/o) SiO_2	B_2O_3	PbO	Al_2O_3	Na_2O	K_2O	CaO	BaO	MgO	OTHER	NOTES
C	**Czechoslovakian glasses**[49] *(continued)*													
	D 47[96]	Ka	87	68.4	2.9		4.7	10.3	5.1	8.5			As_2O_3 : x; no halide	Seal glass for FeNi 50/50 with $\alpha = 86 - 92 \times 10^{-7}$
	E glass	Ka	54	53.0	10.0		15.3	0.8		17.2		3.8		Alkali-free braid glass[51]
	F 46[96]	Ka	95	67.4			2.9	17.7	0.7	9.5		2.0		Soft apparatus-glass
	Fe glass	(Sv)	126.5	45		32		4	14				CaF_2 : 5	Fe-sealing
	K 43	(Ka)	84	72.6			5.95	9.5	4	5.1	0.6	0.9		No longer made
	Kavalier glass	(Ka)		76			0.2	7.2	7.5	9		0.1		No longer made
	Kovar(originally K 705)	Ka	47	66	21		5.0	3	4					Kovar sealing
	LL low-loss glass (formerly K 707)	Ka	32	72.8	22.3		1.1	1.5	1.2	0.8			Li_2O : 0.2; As_2O_3 : x; F : x, Cl : x	Low dielectric loss; cf. Table T 10–2, A1, 7070 glass
	KS (KAVALIER)	Ka	87	75.1			0.6	9.8	3.9	10.8				Technical apparatus[51]
	M glass, Pb glass	Po	94	54.1		29	0.5	5.0	8.4	x			As_2O_3 : 2.8? Sb_2O_3 : 1.48?	For Dumet wire seals
	Mg glass, see Žárovkové sklo	Ko	96.6	70.2			1.5	18.7		4.4	2.1	3.1		Hot-filament lamp bulbs
	Molybdenum MoKa[52]	Ka	50	75.0	10.0		4.9	7.2	1.3	1.6				Mo sealing. must contain no fluorine
	Neon glass	Po		68.7	2.4		4.1	13.3	4.7	6.8				Neon tubes
	O-glass-Svor	Sv	92	54.5		31.5	0.1	3.7	8.5	1.0				Pb glass, pumping stems, foot bead-glass, luminous tube bases
	P 31	Po	52	75.7	11.5		4.3	8.3						Low expansion, chemically resistant type
	Palex	Ka	63	70	5		5.5	8.5	1	5.1		2.2	Zn : 2.8	Press glass, low expansion[51]
	Pb-Koštany	Ko	(92)	55.5		30.7	0.5	4.0	8.4	0.8				Pb glass for tube foot

	Pb-Nižbor	Ni	86	57.7			26.7	1.8	6.0		5.2					As_2O_3: 2.3; Sb_2O_5: trace	Pb glass for tube and lamp feet/bases
	PN	Po	81	66.6 +0.5 −0.4	2.0 + 0.2 − 0.3	—		29 ± 0.5	14.1 +0.3 −0.5		0.4 ± 0.2	5.8 + 0.4 − 0.5	—	—		ZnO: 8.2 +0.4 −0.6	Thermometer glass[53]; $Al_2O_3 = R_2O_3$
	Sial	Ka	46-47	(75)	(7.2)			(5.5)	(6.5)			(1.5)	(4.2)				Hard apparatus-glass; numbers in parantheses from [3]VOLF
				74.6	6.8			6.0	6.6			1.5	4.4				
	Simax	Ka	32	79.8	11.9	—		2.9	4.6		0.3	0.3	—	—			Heat-resistant glass
	Unihost "UH"	Ho	94	68.2— 68.8				2.7— 3.0			18.3—18.5	6		4.1— 4.2			Soft apparatus-glass, luminous tubes, and envelopes for miniature tubes
	WoKa (tungsten)	Ka	40	70.0	14.5		5.5	4.8	1.3		3.2	1.8					W-sealing
	Žárovkové sklo	Ko	96.6	70.2				1.5			18.7	4.4	2.1	3.1			Hot-filament lamp bulbs

	TRADE NAME	α [10^{-7}/°C]	CONTENT (w/o) SiO_2	B_2O_3	PbO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	BaO	MgO	OTHER	FOOT-NOTE
D	**German glasses**													
I	Pre-war mfr., now made in Western Germany													
D 1	Mfr.: ALT, EBERHARD UND JÄGER, Ilmenau (Thüringen); pre-war mfr. see Table T 10–4												comp. not known	
D 2	Mfr.: DEUTSCHE SPIEGELGLAS-GESELLSCHAFT													
	R 51	81	42		50			2	4	0.3	0.3			
D 3	Mfr.: GLASWERK G. FISCHER, Ilmenau (Thüringen); pre-war mfr.													
	Ampullax	85	67	5.5		3.5		10.5	7.5	6				
	Fe seal glass		44.3	2.0		5.0		27.5	8.5	0.3	3.0	6.0	ZnO: 3.5	(75)
	Mo-glass FISCHER	50	63.3	22.6	—	5.4	0.06	6.9	0.17	1.54		trace	(R_2O_3 = 5.5)	
	Transmitter-tube glass		69.0			4.6	0.15	12	7.0	6.9		0.2	MnO: trace	(9)
D 4	Mfr.: GERRESHEIMER GLASWERKE													
	Gerrix glass silk		56	9		16		1.5	0.5	12	1.5	4		
			53.2	7		16		2.3	—	13.4	3	5		(37)
D 5	Mfr.: GREINER UND FRIEDRICHS, Stützerbach; pre-war mfr.													
	R glass		75	7.5		5		6.5		5.7	6			(27)
	SI neutral		70.5	7.7		5.8		6.5	0.7	3.8	2.6			(27)
D 6	Mfr.: E. GUNDELACH (now THÜRINGER GLASUNION), Gehlberg (Thüringen); pre-war mfr.													
	Apparatus glass GUNDELACH 1932	88	65	2		5.5		12	3	7.5	5			
	1939		62.9	—		5.4		10	4.7	6.9	7.5	0.2	Sb_2O_3: 2.0	

TABLE T 10 2 *(continued)*

	TRADE NAME	α [10^{-7}/°C]	CONTENT (w/o) SiO_2	B_2O_3	PbO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	BaO	MgO	OTHER	FOOT-NOTE
D	**German glasses** *(continued)*													
D 7	Mfr.: PÜTZLER; pre-war mfr. Indifferent glass		65	21		4		9	0.5					
D 8	Mfr.: GLASWERK OSRAM, pre-war mfr. at Weisswasser (Oberlausitz), now at Augsburg													
	105 bulb glass, magnesia glass	89	70					17	1	5.5	2.5	4		
			70.3			1.4		16.4	1.0	5.5	2.0	3.4		(75)
	123a (M glass, high-lead)	86	56		31	0.2		4	9					
			56.08		30.6	0.2	0.05	5.03	7.9	0.34		trace	TiO_2:0.03	(1)
			55.9	0.27	29.5	1.0	0.09	4.85	7.43	0.45		0.09	TiO_2:0.25; As_2O_3:0	(11)
			55.0		32.0	1.0		3.8	9.2					(75)
	123b (M glass)	88	55.0		32.0	1.0		4.0	8.0			-		(26)
	140 (white opal bulbs)	89	64.2			3.4		11.0	1.5	4.8			ZnO:8.7; F:6.4	(75)
	362a tungsten sealing	39	(70)	(16)	(6)	(2)			(5)	(0.2)				
			71.7	14.58	5.15	1.91	0.09	2.36	4.20	0.0			R_2O_3:2.00	(1)
			72.05	14.07	6.11	2.21	(31)	4.23	1.12	—				(1) (29)
			71.60	12.10	5.34	5.41	0.14	—	5.46	0.56				(26) (30)
			71.6	14.1	6.1	2.2		4.2	1.1					(75)
	584d medium-hard apparatus-glass	88	65	2		5.5		12	3	7.5	5			(6)
	637h ($T_{\varkappa 100}$ = 300 °C) (30) Mo glass	≈ 48	74.88	8.06		5.78		5.98	—	1.30	3.29	0.11		(26) (30)
			74.9	8.1		5.8		6.0		1.3	3.3			(75)
	idem, older mfr.	48	73.2	9.4		6.6		6.4	—	—	4.4	—		(27)
	712b (30) (W glass)	42	75.16	6.90		3.31		4.29	6.93	0.56	0.46		ZnO:2.05	(26)
			75.2	6.9		3.3		4.3	6.9	0.6	0.5		ZnO:2.1	(75)
	742 (phosphate glass) (30)	31	51.0	1.3		26.3		0.7		8.9	4.7	4.3	P_2O_5:4.0	(26) (30)
	idem, earlier mfr.	31	51.3	1		25.5		—		8.5	5.3	4.2	P_2O_5:4.6	(38)
	742g tungsten glass		51.2	6.7		18.4				6.0	11.4	2.0	P_2O_5:4.3	(75)
	743b (Pb-free Dumet glass)	91	61.5	1.0		0.5	—	7.0	8.0	1.3	11.0	0.7	ZnO:7.0; F:2.0	(26) (75)
	756 Fernico seal glass	48	67	22		2			6.5					(3)
	756b Kovar seal glass	46.8	64.75	21.3		5.90		6.9	—	0.47		0.53		(1)
	Magnesia glass (hot-filament lamps) see also 105 glass	≈ 90	70.3			1.4		16.4	1.0	5.5	2.0	3.4		
			70			2.0			7	5.5	2.0	3.5		
	tungsten sealing glass see also 742 glass	≈ 40	51.2	6.7		18.4		—		6.0	11.4	2.0	P_2O_5:4.3	(26)

D 8	tungsten sealing glasses with very high $T_{\chi 100}$ (588°)		61.9		18.5			10.2		9.4			(75)
			77.0		16.4			3.3		3.3			
			44.7		13.4			35.1		6.8			
D 9	Mfr.: GLASWERK SCHOTT UND GEN. (so-called Jena glasses); mfr. partly in VEB GLASWERK JENA, Eastern Germany, partly in the Glassworks at Mainz, Western Germany												
	16^{III} (standard thermometer glass)	80	66.5	0.9	3.85		14.8	0.01	7.2	0.17	ZnO:6.35		(28) (53)
			67.5	2.0	2.5		14.0	0.01	7.0		ZnO:7.0; Mn_2O_3:0.2		(28)
			67	2.0	2.5		14.5		7.0		ZnO:7.0		(90)
	20 (apparatus glass 20) see 3072^{III}												
	59^{III} (Jena glass)	60	71.95	12	5		11				Mn_2O_3:0.05		(9)
			73	10	6		10	0.1	0.4	0.2			
	102^{III} (Fe sealing)		57.0		12.0			26.0			ZnO:5.0		(75)
	1003^{III} (iguition glass)		67.3	6.3	5.8		2.7	2.4	7.4	7.6 0.2			(27) (55)
	1447^{III} (seal glass for Mo up to 3 mm dia.)	50	64.6	10.2	4.9	0.18	7.4	1.35	0.5	0.18	ZnO:10.8; As_2O_3:0.15		(1)
			64.5	10.8	4.4		7.5	0.4	0.6		ZnO:11.1		(26)
			64.3	12	4		7.5	—	—	— —	ZnO:12; As_2O_3:0.2		(27) (90)
			64.6	10.9	4.9		7.4	0.4	0.5	0.2	ZnO:10.8; As_2O_3:0.2		(39)
	1483^{III} (white Fiolax glass)		67.5	8	11.5	0.1	7.5	0.2	5.9				(9) (55)
	1569^{III} (ignition glass)		57.4	3.5	23.2		1.9	0.5	4.7	8.7			(27) (55)
	1639^{III} (intermediate glass for Mo > 3 mm dia.)	49	71.0	20.0	1.0		8.0 (7.8*)				As_2O_3:0.2		(58) (*) see (75)
	1646^{III} (W glass) intermediate glass for W > 3 mm dia.	41	70.3	16	2		5.5	—	—	3 —			(27)
			73.3	16.0	2.0		5.5			3.0	As_2O_3:0.2		(75) (90)
	1650^{III} (Minos glass) $\tan\delta = 5\text{—}6\times10^{-4}$	88	45.5	43.9	0.6		6.0	3.0	0.3	0.5	(R_2O_3:0.6)		(27)
			46.0	45.5	—		3.5	5.0	—	—			(58)
	2877^{III} see 3072												
	2954^{III} (Jena glass)	60	66.5	9.0	10		8.5		6.0				(58)
	2962^{III} (Pt seal glass)	80	75	4	2		13	4	2				(27) (90)
	3058^{III} (Supremax)	33	55.3	7.4	22.9	0.13	0.6	0.38	4.7	8.5			(1)
			55.0	7.9	22.7		0.6	0.3	4.6	8.4	As_2O_3:0.5		(14)
			56.80	6.55	21.98		1.29		4.53	0.64 7.76			(26)
			53.0	10	21				5	10	As_2O_3:1.0		(90)
	Mfr. 1951		56.8	6.6	22.9		1.3		4.5	0.6 7.8			(56)
	3061^{III} (Na-resistant)		—	22.5	25.0			1.5	18.0	33.0			(90)
	3072^{III} (apparatus glass 20)	46	75.6	8.98	5.04	0.10	5.2	1.2	0.44	3.8			(1)
			75.7	6.9	5.1		6.2	1.2	1.3	3.6			(26)
			76.4	8	4		6.5			4.0	CaF_2:0.75; As_2O_3:0.35		(90)
			75	8	6.5		6	1	1	3.1			
			76	8.5	4.5		5.5	1.0	0.3	4.0	As_2O_3:0.3		(11)
			75.3	7.6	6.2		5.7	0.8	1.1	3.5			(37)
	idem (1951 analysis)		74.60	9.63	5.48		5.44	—	1.00	3.74			(26) (56)

TABLE T 10–2 *(continued)*

	TRADE NAME		α [10^{-7}/°C]	CONTENT (w/o) SiO_2	B_2O_3	PbO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	BaO	MgO	OTHER	FOOT-NOTE
D	**German glasses** *(continued)*														
D 9	3079[III] (sealing Pb-glass, tan $\delta = 10 \times 10^{-4}$)		81	52.75	5	30			4	8				As_2O_3:0.3	(27) (90)
	3891[III] (Duran glass)		37	73.8	13.4		4.1	0.07	4.6	0.24	0.3	3.1	0.2		(1)
				74.5	14.0		3.5		4.5			3.0		As_2O_3:0.3	(75) (90)
				74.0	14.0		3.5		3.5	1.0	—	3.0		As_2O_3:1.0	(14)
	4116[III] Mo Uviol glass		53	75.0	12.0		2.0	(0.02)		11			(0.1)		(58)
	4172[III] (boron free)		33	60			15				8	5		ZnO:12; As_2O_3:0.3	(38) (55) (90)
	4225[III] Rasotherm glass			80	13		2		4						(26)
				78.0	14.0		2.5		5.5						(60) (56)
	5067[III] (Fiolax, new)			64.8	0		6.0		4.8	1.2	5.0	7.0	2.7	ZnO:8.0; As_2O_3:0.3	(14) (57)
	Fiolax, earlier type			66.1	7.2		10.4	0.14	7.4	2.9	6.3		0.4	MnO:0.12	(27) (55)
	8039 (W sleeving glass) (32)			76.80	11.72		4.30		5.24	0.30	0.56	0.40	0.12		(26) (32)
	Joining glasses (SCHOTT)		(20 to 100 °C)												
		C 1	8	96.0	1.8		2.0		0.2						(27) *) see (75)
		C 2	9	92.0	3.8		4.0		0.2 (0.4*)						
		C 3	12	88.0	5.7		6.0		0.3						
		C 4	15	85.8	7.4 (7.0*)		5.5		0.7			0.6			
		C 5	21	83.6	8.8		5.0		1.4			1.2			
		C 6	26	81.3	10.3		4.5		2.1			1.8			
		C 7	30	79.0	11.8		4.0		2.8			2.4			
		C 8	35	76.8	13.2		3.5		3.5			3.0			
		C 9	38	74.0	14.0		3.5		4.5			3.0		As_2O_3:1.0	
		C 10	48	76.0	8.5		4.5		6.5			4.0		As_2O_3:0.5	
		C 11	50	64.0 (64.3*)	12.0		4.0		7.5					ZnO:12.0; As_2O_3:0.2	
		C 12	60	72.0	12.0		5.0		11.0						
		C 13	62	67.3	8.5		4.0		8.3	1.2	5.0	4.0		ZnO:1.5; As_2O_3:0.2	
		C 14	73	63.8	20.0		1.0		15.0					As_2O_3:0.2	
		C 15	73	66.8	11.0		3.0		14.0		2.0			ZnO:3.0; As_2O_3:0.2	
		C 16	80	75.0	4.0		2.0		13.0	4.0	2.0				

D 10	Mfr.: SCHÜBEL; pre-war																
	Normal glass			61			3.5		12	7.5	7.5		0.5				
	Special glass			62.5		0.5	3.5		7.5	12.5	8	4	2				
D 11	Mfr.: SENDLINGER OPT. GLASWERKE, Berlin-Zehlendorf																
	96/2 (Fernico sealing)		(≈ 50)	70.60	11.75		4.66		10.70	1.66	0.36		0.10				[26]
	S 21/12 (W sealing glass, "Ignal")		(≈ 40)	68.30	8.05	5.84	3.36		4.69	0.71	0.28	(4.0*)		Sb_2O_3:3.95; ZnO:3.30			[26] (*) see [75]
	V 315 m (Mo sealing)		61	70.54	10.60		4.57		5.32	1.25	0.58		0.15	ZnO:6.57			[26]
	V 320 w (W and ceramic sealing)		52	73.02	4.41	7.42	4.49		5.76	0.81	0.26 (0.4*)			ZnO:3.51			[26] (*) see [75]
D 12	Mfr.: SOPHIENHÜTTE RICHARD BOCK, Ilmenau; pre-war mfr.																
	S-I neutral yellow (ampoule glass)		51	65.7	6.25		5.5	2.02	9.64	1.43	3.36	1.73		MnO:2.80; ZnO:2.12			[9]
	Fe sealing glass		> 110	66.1	6.85				7.69	1.28	5.54	3.60	0.14	ZnO:2.46			[26]
D 13	Mfr.: RUHR A. G.-GLASWERKE																
	AR glass		≈ 90	69.52	1.4		4.24		10.82	5.27	7.84			} (lead-free Dumet wire sealing glasses)			[26]
	LR glass		≈ 90	68.5	0.4		3.6		17.7	2.0	7.5						[26]
	MGR glass		≈ 90	70.9			3.24		15.4	1.22	4.78	1.56	2.90				[26]
D 14	Mfr.: GLASWERK-WERTHEIM, Wertheim/Main (re-established in Western Germany after war)																
	see Table T 10-4, D14			glass compositions not known													
D 15	Mfr.: various(4); pre-war mfr.																
	Eutectic W sealing glass $T_{\varkappa 100} = 588°$		≈ 38	61.9			18.5				10.2		9.4				[26] [33]
	Fiber glass			50.2	14.1		13.3		1.3	0.3	15.9		4.4				[2]
	Kovar sealing glass		≈ 50	66.0	24.0		2.0		8.0								[26]
	Na vapor resistant glass			22.9	41.3		21.2	0.1	4.8	0.8	9.0						[9]
	Standard lead-potash glasses ("lead crystal glass")			53		33				14							
	Standard lime-potash glasses			71 78			0.3	0.2	7	18 10	11 5						
	Standard soda-lime glasses			75.5 77			0.2	0.2	12.9 12	3	11.6 8						
	Opal glass			68 68.4			3 3.9		6 6.8	1 1.8	5 5.4			ZnO:10; F_2:7 ZnO:9.8; F_2:6.8			[7]
	Thüringer apparatus glasses	standard		68		3.5			14	8.5	6						
		low melting		70.0		3.3		0.2	14.0	6.2	6.3						
		medium hard		68.6	3.2	3.3			12.3	5.3	7.3						
		idem, with high BaO content		62.6	1.9	4.3			10.2	6.0	7.1	7.9					

TABLE T 10–2 *(continued)*

	TRADE NAME	α [10^{-7}/°C]	CONTENT (w/o) SiO_2	B_2O_3	PbO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	BaO	MgO	OTHER	FOOT-NOTE
D	**German glasses** *(continued)*													
D 15	UV-transparent W glass		66.5	23.8		5.3		2.5	—	0.7				(26)
	tungsten sealing glass		72	14.1	6.1	2.2		4.2	1.1					
II	Now made in Eastern Germany													
D 16 to D 25	Various VEB's (see Table T 10–4)		unknown composition; alterations may have been made in the pre-war products (D 1, D 3, D 5, D 6, D 8, D 9, D 12) (KALSING)											
E	**English glasses**													
E 1	Mfr.: BRITISH THOMSON-HOUSTON, Rugby	50 to 400 °C												
	C 9 (W glass)	36.5	74.6	18	—	1.0		4.2	1.7		0.3			(23)
			75	18.3	—	1.1		3.4	1.9	0.3				(19)
			75.0	18.2		1.0	0.1	3.4	1.9	0.3				(60)
	C 11 (Mo glass)	45.5	73	14		2.3		7.5		x		x	Σ x : 3.0	(23)
			73.0	14.0		2.3				3.0	7.5(?)			(75)
	C 12 (Dumet glass)	91	56		30	1.3		4.0	8.0					(75)
			57.4		29.3	1.3		3.9	7.6					(23) (24)
			57		30	1		12						(25)
			57		30	1		5	7					(27)
	C 13		57		29.3	1.3		3.9	7.8					(27)
	C 14 (W glass)	39	58.5	3.0	—	22.5		—	0.8	6.3		8.9		(23)
	C 18 (Mo glass)	≈ 50	57	4		21.8				7.8	1	8.9		(27)
	C 19 (CrFe glass) soda lime	95	72			1		17.3			9.4			(25)
	C 22 (soda-lime)	104	67.5	0.7		3.9		20.7			6.7			(25)
	C 31 (FeCr glass)	97	52		30	1		—	14.5	2.5				(23)
	C 37 (Mo glass for high pressure Hg lamps)	42.5	55.8		5.1	23.0				13.0	3.1			(95)
	C 38 (intermediate glass)	≈ 32	68.5	30				1.5						(25)
	C 40 (Kovar glass)	48.5	66	24		2		8						(22) (23)
			65.9	24		1.8		3.8	4.2					see also (39)

E 1	C 41 (Pb-free glass for sealing to metal)	128	x		0.0!			x	x				ZnO:x	(43)
	C 46 (Mo glass, high softening point)	43	54.5	0.0		23.5				11.3	6.3	0.5	P_2O_5:3.8	(95)
	C 53 (W glass)	≈ 35	68.5	30					1.5					(23)
	C 54 (Pb glass, cf. C 12)	94.5	x		≈ 20!			x	x		x			(43)
	C 73 (CrFe glass)	98.5	x		≈ 20!			x	x		x			(43)
	C 76 (Pb free, Fe-sealing)	115	48.2		0.0!			16.8			30		CaF_2:5	(24) (25)
	C 93 (seals to mica and to C 12, C 19 or C 54)	50—200 °C 76	x	x	x									(43)
	D 2 } Pb-free, Fe sealing glasses	0—400 °C 139	45		—			6.0	14.0		30		CaF_2:5.0	(78) (79)
	D 5 } Pb-free, Fe sealing glasses	122	45		—			6.0	14.0		15		CaF_2:5.0; ZnO:15	(78)
	D 6 } Pb-free, Fe sealing glasses	133	45		—			6.0	14.0		23		CaF_2:5.0; ZnO:7	(78)
	D 7 } Pb-free, Fe sealing glasses	127	45		—			6.0	14.0		19		CaF_2:5.0; ZnO:11	(78)
	R 48 intermediate glass	20—300 °C 13	83.5	12.5		4								(25)
	R 49 intermediate glass	20—300 °C 18	78.5	17.5		4								(25)
	R 50 intermediate glass	20—300 °C 23	74.5	17.5		4					4			(25)
	Pb-free glass for pressed glass seals	≈ 93	48.2		—			5.0	11.8		19		CaF_2:5.0; ZnO:11	(78)
E 2	Mfr.: CHANCE BROS. LTD.													
	GH 1 (Hysil) } GH A }	33	80.4	12.4		2.7		4.2		0.3				(19)
			80.0	12.0		3.0	0.1	3.9	0.3					
			80.6	12.2		2.7	0.06	4.2	—	0.12				(60)
	GS 1 (Intasil) W glass, see also GSD	38	74.5	13.0		4		5		0.5	3.0			(19) (23)
	GS 3 (Kovarglass) see also GSB	54.5	67	21		4		3	4.6				Sb_2O_3:0.4	(19) (24)
	GS 4 Mo glass	44	76	10		4		6		1	3			(19)
			76	10.5		4.0		6.0		x	3	x	Σ x:0.5	(19) (23)
	GSB (GS 3) Kovar glass	54.5	67	21		4		3	4.5				Sb_2O_3:0.02; F < 0.02; NaCl < 0.005; SO_3:0.10	(17)
	GSD (W glass), see also GS 1	10—100 °C: 38.7[41]	78.60	12.87		2.56		4.90		0.01	0.03		NaCl:0.13; $As_2O_3 + Sb_2O_3 < 0.07$	(17)
	GW 1 soda-lime		74			1		16		7			Sb_2O_3:1.3	(19)
	GWA (GW 7)	87	73.8	trace		1.62	0.044	15.33	0.46	7.04		trace	Ti_2O_3:0.027; Na_2SO_4:0.87; As_2O_3:< 0.002; Sb_2O_3:0.42; NaF:0.01; NaCl:0.11	(17)

TABLE T 10–2 *(continued)*

	TRADE NAME	α [10^{-7}/°C]	CONTENT (w/o) SiO_2	B_2O_3	PbO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	BaO	MgO	OTHER	FOOT-NOTE
E	**English glasses** *(continued)*													
E 2	GWB (GW 2) Pb-glass	86	58.4		29.0	0.5	0.041	5.8	4.9	0.5			TiO_2:0.028; Sb_2O_3:0.6; NaCl:0.061; MnO_2:0.1; F:< 0.005; SO_3:0.034	(17)
			60		26	0.1		8	5				Sb_2O_3:0.5	(19)
E 3	Mfr.: GEC, Wembley													
	B 8 (hand-blown; similar to X 8)	96.5	70.0	0.50		2.0		16.5	1.0	4.75	1.0	3.5	Sb_2O_3:0.75	(42)
	FCN (Fernico/Kovar sealing)	48	66.0	24.0		2.0		4.0	3.5	0.5				(42)
		51	66	24.5		1.9		4.3	3	0.4				(23)
	H 26		54.3	7.5		22.0				13.3	3.0			(75)
		43	54	8		21				14	3			(23)
	H 26 X (Mo sealing) for high-pressure Hg lamps; alkali-free	46	54.25	7.5		22.0		0.0	0.0	13.25	3.0			(95)
	HH (Mo sealing glass)	47	73	14.4		3		2.4	4.2	3				(19)
			72	13.0		4.0		3.5	4.0	3.0	—	0.5		(21)
	HR 9 (pressware)	51.5	68.5	13.5	6.0	2.5		7.5		0.75	1.0	0.25		(42)
	L 1 (soft Pb glass) for Dumet sealing	91	56.5	0.2	30.0	0.8—1.0		5.1	7.2					(19) (23)
			56		30.0	0.3		5.2	7.5	0.5		0.3		(75)
			56.0		30.0	1.0		5.2	7.5	0.5		0.3		(21) (24) (42)
			56.6		30.2	0.8		5.1	7.2					(60)
	L 14 (CrFe sealing glass)	98	53		29.7	0.8		3.8	10.3	2.1 (3.1(*))				(23) (*) see (26)
	M 6 ("white neutral")	≈ 73	67.0	7.5		8.5		8.7	4.0	4.0		0.3		(42)
	Na 10 (Na-vapor resistant)	similar to X 8	8.0	48.0		24.0	< 0.01	14.0		6.0				(21) (42)
	RL 16 (Fe sealing)	114	51	10		10		18.5	2.0	5.5			F_2:3.0	(23)
			51	10		10		18.5	2.0	1.6			CaF_2:5.0	(75)
	SS 3 (high elec. resist. sheathing glass)	94	66	2.0		0.72		6.3	9.9	0.44	15.0			(21)
	W 1 (W sealing glass)	38	75.5	16.3		2.2		4.0	2.0					(42)
			74.5	17		2.0		4.5	2.0	0.2				(23)
			74.8	16.3	—	2.2		3.9	1.9	—				(60)

| | | |

TABLE T 10–2 *(continued)*

	TRADE NAME	α [10^{-7}/°C]	CONTENT (w/o) SiO_2	B_2O_3	PbO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	BaO	MgO	OTHER	FOOT-NOTE
H	**Dutch glasses**													
H 1	Mfr.: PHILIPS GLOEILAMPENFABRIEKEN N. V., Eindhoven													
	lead glass 111	92	61.5		21.7	1.79[15]		8.6	6.0	0.39		trace		
	lead glass K 1 A	95	56.0		29.4	1.1		4.1	8.3	0.9				
			57		27.4	1.67[15]		8.5	4.8	0.39		0.03		
			57.1	1.5	29.4			4.9	7					(27)
	Ce-containing panel glass for TV tubes		66	2	—			5	10		15		CeO_2:2	(91)
	Fe sealing glass		45		32			6	14				CaF_2:5	(75)
J	**Japanese glasses**													
	Jap. Fe sealing glass Ikeda	124	45.5		30.3	3.7		3.4	15.2	1.2		0.2		(26)
Oe	**Austrian glasses**													
	Mfr.: MOOSBRUNNER GLASFABRIKEN A. G., Vienna VI (pre-war mfr.)													
	Pb-free bulb glass		70					17	1	5.5	2.5	4		
	lead glass N (915a)	100	56		31	0.2		4	9					(26)
	Fe sealing glass L 1	115	55	2	6		1.8	13.5	7	4	6		TiO_2:5	
	idem Z 601a	119	57.8			4.1		12.0	9.7	6.9	7	2.4		
	W 2 Pb-glass	82	42		50	0.1		2.1	4.2	0.3	0.3			

	TRADE NAME	CONTENT (w/o) SiO_2	B_2O_3	PbO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	BaO	MgO	OTHER	FOOT-NOTE
P	**Polish glasses**												
	lead glasses for Dumet wire sealing	56.6	—	31.9			3.9	7.9					(64) (73)
		55.7	—	31.2			4.6	8.5					(64) (74)
		65.0	—	12.9	0.7		8.4	6.5	2.7	3.8			(64)

	TITLE OF GLASS FORMER	MODERN	CONTENT (w/o) SiO_2	B_2O_3	PbO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	BaO	MgO	OTHER	FOOT-NOTE
S	**Russian glasses**													
	Ba-Li glass	713	67.5			5.0	< 0.9	7.0	7.0		12.5		Li_2O: 0.6	(93)
	BB apparatus glass, boron-free		69.06			3.88		9.42	7.14	8.50		2.00		(27) (63) (67)
	BD-1 barium glass	S-90-1	69.5				< 0.3	[12.0] 12.5	4.0	5.5	5.0	3.5		[] from (84) (63) (68) (94)
	Pb-free glass		73.6			3.67			17.23		5.37			(65)
	Pb glass		61.5		29.4		0.8	3.0	9.4					(65)
	Durobax		65.7	7.8		6.0		2.0	2.9	7.8	6.8	1.0		(63) (71)
	Jena type glass		64.7	10.9	—	4.2	0.25	7.5	0.37	0.63	—	0.21	ZnO: 10.9; MnO: 0.01; As_2O_3: 0.14	(63) (70)
	Bulb glass		72.43				1.08	15.3		0.19	5.09	5.60		(65)
	Bulb and tube glasses		67.4	—	—	0.1	0.7	7.3	8.7	0.2	3.1	11.8	—	(65)
			71.1	—	—	0.1	0.4	6.1	10.0	0.2	3.8	7.5	—	
			70.0	—	0.64	0.5	—	5.9	9.15	1.67(72)	4.28	8.4	—	
			60.1	—	—	0.3	0.6	—	15.90	0.36	2.83	19.8	—	
			68.8	—	—	0.22	2.57	—	21.9	10.2	6.96	—	—	
			69.8	—	0.21	0.20		5.04	14.69	3.14(72)	5.35	—	—	
			71.56	—	1.2	3.86	0.99	—	15.78	0.36	6.25	—	—	
	Mazda glass		57.6	—	—	25.0	—	—	2.0	7.4	—	8.0	—	(63) (71)
	Pyrex I		80.5	12.0	—	2.0	—	4.0	1.0	0.5	—	—		(63) (70)
	Pyrex II		79.61	12.12	—	1.93	0.17	3.68	1.74	0.43	—	0.17		(63) (70)
	Pyrex-Wo-glass	P-15	78.5	15	—	2.0	—	3.0	1.5					(94)
	Tube glass		68.9	—	—	0.3	0.6	15.5	—	0.4	5.2	8.9		(65)
	Sverchpireks (Pyrex type)		85.4	8.3	—	2.0		3.5				0.3	P_2O_5: 0.4	(75)
			85.4	8.32		1.03		3.54				0.36	WO_3: 1.00	(27)
	White glass		72.0	—	—	1.5		13.5	0.5	10.0		2.5		(63) (67)
	Wo tungsten glass		78.5	14		1		5.5	1.1					(27)
	ZS 4 Pb glass	S-88-4	55.3	—	30.0	1.7	< 0.3	3.8	9.2	—	—	—	—	(59) (84)
	ZS 5 K	S-49-5 K	66.9	20.3	—	3.5	< 0.04	3.9	5.4	—	—	—	—	(84)
	ZS 5 Mo		68	20	—	3	—	4	5					(27) (59) (63) (68) (75)
	ZS 5 Na	S-49-5	67.5	20.3	—	3.5	< 0.04	8.7	—	—	—	—	—	(84)
	ZS 8 Mo	S-48-8	66.5	23	—	3	< 0.05	3.7	3.8	—	—	—	—	(27) (63) (68) (94)
	ZS 9		68.8	26.5	—	1.6	—	2.5	0.6	—	—	—	—	(84)

TABLE T 10–2 *(continued)*

	TITLE OF GLASS FORMER	MODERN	CONTENT (w/o) SiO_2	B_2O_3	PbO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	BaO	MgO	OTHER	FOOT-NOTE
S	**Russian glasses** *(continued)*													
	ZS 11		74.9	18.0	—	1.0	—	4.2	1.7	—	0.3	—		(94)
	No. 2	S-89-2	71.9	—	—	—	< 0.3	16.1	1.0	5.5	2.0	3.5		(84)
	2 soft bulb glass 59, B-free		72.6			4		14.5		8.7				(27) (63) (67)
	VI-V Pb glass		66.0	—	14.5	1.0	—	9.0	7.0	2.5	—	—		(63) (68)
	Original-VI-B		67.2	—	13.9	0.8	—	8.7	6.6	2.6	—	—		(64) (68)
	10 Pb glass for bulbs		73.33	—	5.37	—	—	11.15	6.0	4.15	—	—	—	(66)
	12 Pb glass		55	—	30	—	—	3.8	9.2	0.26	—	0.04	P_2O_5: 1.7	(63) (68)
	16 for Dumet		70	—	10.4	—	—	11.0	4.8	3.8	—	—		(64) (69)
	16 Pb glass, for electrical work		69.58	—	10.20	—	—	10.59	5.69	3.94	—	—	—	(66)
	No. 16		67.5	2.0	—	2.5		14		7.0			ZnO: 7.0	(94)
	17 W glass	S-39-17	73.0	16.5	6.0	—	< 0.04	3.0	1.5	—	—	—	—	(59) (84)
	23 laboratory glass		68.39	2.66	—	3.89	—	9.42	7.14	8.51				(63) (67)
			69.6	2.8	—	4.0	—	9.0	7.7	6.9	—	—		(84) (94)
	29 white opal glass													(59)
	35 Mo-glass		63	24.9		1.5		9.1	1.5					(27) (63) (68)
	36 glass	S-82-36	71.5	—	—	1.8	< 0.3	11.5	1.2	14.0	—	—		(84)
	40 high softening point bulb glass		57.6	—	—	25.0		—	2.0	7.4	—	8.0		(59) (34)
	46 Mo-glass		68.2	16.5		4		6					ZnO: 5	(27)
			68.25	16.5		4.0		6.0					ZnO: 5.0; As_2O_3: 0.25	(63) (68)
		S-47-46	68.5	17.2	—	2.5	< 0.05	6.8					ZnO: 5.0	(84) (93)
	55 UV bulb glass		72.81			1.19		16.44	0.78	5.42		3.36		(27) (59) (66)
			72.5			1.5		15	2.0	5.5		3.5		(94)
	59 thermometer glass		72	12		5		11						(63) (67)
	59 Pb-glass for automatic glass-working machinery		69.78	—	16.12	—	—	8.42	7.85	1.84				(65) (66)
	71 magnesia hot-filament lamp glass		73.62	—	—	—	—	17.0	—	5.46	—	3.91		(63) (68)
	71 Pb-free, hot-filament lamp glass		72.49	—	—	—	—	15.89	1.33	5.36	1.43	3.50		(27) (66)
	82		74.0	—	—	—	—	16.6	—	5.8	—	3.6		(94)
	83 Pb-free lamp glass		72.58					13.94	3.95	5.56		3.97		
	112 Ba glass		71.5					10.0	5.5	4.5	7	1.5		(63) (68)

	TRADE NAME	CONTENT (w/o) SiO_2	B_2O_3	PbO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	BaO	MgO	OTHER	FOOT-NOTE
401		68.1	4.0	—	4.0		9.4	5.2	7.2		2.1		(94)
402		67.9	—	—	3.9		11.2	6.9	8		2.1		(94)
846 standard laboratory glass		74.0	3.0	—	3.0	—	10.0	—	6.0	—	4.0		(63) (67)
		73.87	2.74	—	4.25	—	9.38	—	5.96	—	3.67		(27)
	S-88-11	71.0					9.8	8.2	5.5	2.0	3.5		(94)
	S-88-13	69.5	2.0	—	—	—	11.0	6.5	5.5	2.0	3.5		(93)
U	**Hungarian glasses**												
	Mfr.: TUNGSRAMWERKE, Budapest												
	B magnesia glass												
	M 28 GrFe press glass												
	M 32 Pb glass for Dumet												

Footnotes to Table T 10–2

(1) Specific analyses; values in ( ) are nominal ones taken from mfr.'s data or from the literature.
(2) Average of four similar products.
(3) "Pyrex" means generally CORNING borosilicate 7740, and "Nonex' means 7720 (see Table T 10–4, Al). It should be noted, however, that these terms, and "Vycor", are the general trade-marks of about 150 different types of glass, but not of precisely specified glasses (KOHL, HELDMAN).
(4) Literature data; mfr. not named.
(5) For mass-production by machines.
(6) Like GUNDELACH apparatus glass.
(7) [3]SPÄTE.
(8) [1]DALE.
(9) LAPORTE.
(10) [1]DOUGLAS.
(11) Glass for pressed seal-ins in Fe rings (see ADAM, [2]ESPE).
(12) Similar to SCHOTT standard thermometer glass 16^{III}.
(13) Similar to CORNING 7050.
(14) [1]SCHMIDT.
(15) Inclusive of TiO_2.
(16) [1]DANZIN.
(17) From Firm's catalogue.
(18) [1]HULL.
(19) YARWOOD.
(20) BLACK (Ce content to prevent blackening by X-rays).
(21) MANNERS.
(22) [1]ESPE.
(23) PARTRIDGE.
(24) [2]ESPE (sealing glass for ferritic CrFe).
(25) [1]DALE.
(26) KALSING.
(27) [1]VOLF.
(28) Because of absence of K_2O, it is not radioactive; hence is suitable for Geiger counters.
(29) Original OSRAM glass (see KALSING).
(30) Glass made by the present-day GLASHÜTTE EINHEIT (VEB), formerly OSRAM at Weisswasser. Not the same as OSRAM glass of the same title, according to KALSING.
(31) Not determined.
(32) Intermediate glass between tungsten and Duran 50, made by SCHOTT UND GEN. at Zwiesel, not at Jena.
(33) Osram glass "742" and Schott glass "Supremax" were developed from this glass by introducing B_2O_3.
(34) Does not soften below 980°!
(35) [2]HOOD.
(36) This glass is made by many other mfrs. (in some cases with small variations in composition) and produced as "M-glass".
(37) THIENE.
(38) DOLEŽAL.
(39) [1]STANWORTH.
(40) [2]SCHMIDT.
(41) Guaranteed to vary only between the limits 38.0 and 39.4×10^{-7} (1/°C).
(42) According to OSRAM-GEC.
(43) According to BRITISH THOMSON-HOUSTON.
(44) Absorption in the I.R.: 90%; in the visible: 5%.
(45) Absorption in the I.R.: 83%; in the visible: 10%.
(46) According to BARR (p. 192): MgO incorrectly cited there instead of Li_2O.
(47) From recent analysis.
(48) No Al_2O_3 should be present, thus should only be melted down in quartz glass pots or ones lined with Pt.
(49) From Výzkumný sklářský ústav, Hradec Králové.
(50) Mfr.: Ho: ŘETENICKÉ SKLÁRNY, Hostomice; Ka: SKLÁRNY KAVALIER, Sázava n. Sáz; Ko: ŘETENICKÉ SKLÁRNY, Koštany; Ni: PODĚBRADSKÉ SKLÁRNY, Nižbor; Po: JABLONECKÉ SKLÁRNY, Polubný; Sv: SEVEROČESKE SKLÁRNY, Svor.

[10.1]

Footnotes to Table T 10–2 *(continued)*

(51) Usable in vacuum work but not proved for metal sealing.

(52) Earlier analysis.

(53) SCHOTT glass 16[111] has no K content and is therefore very suitable for making Geiger counters, although it is not so suitable for complex glass-blowing operations because of the high ZnO content. A similar glass (not quite so K-free) is PN (see this table, C).

(54) [2]DANZIN.

(55) Older types, from data of VEB SCHOTT UND GEN. at Jena, not made today.

(56) Made by VEB SCHOTT UND GEN., Jena, Eastern Germany.

(57) B_2O_3-free ampoule glass dating from wartime, according to VEB SCHOTT UND GEN. (Jena) not made today.

[10.1] (58) Data given in correspondence from VEB GLASWERKE SCHOTT UND GEN., Jena.

(59) [1]KNAPP.

(60) REIMANN.

(61) Trade-names of GDR glasses are sometimes also those of FRG products. As a result of the independent development and manufacture in both areas since 1948, compositions and properties of German glasses of the same name but different sources can diverge widely.

(62) Made pre-war and in World War II.

(63) VESELOVSKIJ.

(64) BERINSON.

(65) KITAIGORODSKIJ.

(66) Theoretical composition.

(67) Made by DRUŽNAJA GORKA.

(68) Made by SVETLANA.

(69) Made by MOSKAUER GLASFABRIK.

(70) Made by POBEDA TRUDA.

(71) Made by LENZOS.

(72) With Fe_2O_3.

(73) Produced in 1949.

(74) Produced in 1953.

(75) [2]KNAPP.

(76) Matches a ceramic of 80% MgO, 10% clay, 10% lime.

(77) So-called "neutral glasses", made by PITTSBURGH PLATE GLASS CO.

(78) [5]STANWORTH.

(79) Devitrified in 24 hr test in range 700—920 °C.

(80) Devitrified in 48 hr test in range 650—775 °C.

(81) Cf. the derived glasses D2 to D7 of the BRITISH THOMSON-HOUSTON CO. in this table, E 1.

(82) [4]HULL.

(83) [3]VOLF.

(84) BORŠČEVSKIJ.

(85) [3]NORTON.

(86) Cf. also Table T 11–1 and Chapter 11.

(87) Fluorine is present in small amounts according to the following furnace charge: sand, 350; H_2BO_3, 235; KNO_3, 19; $NaSiF_6$, 26 parts by weight.

(88) Spectrographically determined, only qualitative.

(89) American mfr. unknown, glass similar to "542".

(90) WHEAT.

(91) [3]GIER.

(92) HAGY.

(93) KOROLEV.

(94) LJUBIMOV.

(95) HILLIEB.

(96) Earlier type, no longer made.

TABLE T 10-2 A. COMPOSITION OF SOME COMMERCIAL BORATE AND PHOSPHATE GLASSES (NO SiO_2 CONTENT)

POS.	MFR.'S DESCRIPTION	α [10^{-7}/°C]	CONTENT (w/o) P_2O_5	B_2O_3	PbO	Al_2O_3	FeO	Na_2O	K_2O	CaO	BaO	MgO	OTHER	AUTHOR
1	LINDEMANN (lithium borate) glasses[1]			16									$Li_2B_4O_7$:81; BeO:3	
				14									$Li_2B_4O_7$:83.5; BeO:2.5	LINDEMANN
				64									Li_2O:20.7; BeO:15.3	[2]KNAPP
1a	Russian lithium borate glass			80									Li_2O:10; BeO:10	[2]KNAPP
2	Na-vapor resistant glass (cf. Table T 10-17B)			36		27					27	10		[2]SCHMIDT
				60		15		13		12				?
3	phosphate glass for Cu and Fe sealing (BRITISH THOMSON-HOUSTON)		33.5	7.0	30.0	15.5		14.0						KALSING
			33.5	14.0	23.0	15.5		14.0						[2]KNAPP
4	IR-absorbing glasses, colorless I[2]		70.7	4.0		10.0	2.5		10			4	ZnO:1; As_2O_3:0.3	[2]BERGER
	II[3]		40.0	30.0		10.0	2.5		10			10		
5	UV-transparent black glass		67			4				5.9	20.1		CoO:2.0; NiO:1.0	HOOLEY
6	High insulation resistant phosphate glass No. 14		33.1	14.0		15.5				9.0	12.4	16.0		[3]STANWORTH
7	HF-acid-resistant phosphate glass		72			18							ZnO:10	PINKUS
7a	*idem* (HAVERFORD GLASS CO.)		77	5		11							ZnO:7	[3]NORTON
8	X-ray shielding phosphate glass	see Table T 10-11												
9	Corex phosphate glass 9700 (CORNING)	see Table T 10-2, A 1												
10	lead-borate glass (G E Co. USA)		—	22	78									[3]NORTON

[1] All components free of water of crystalization: fused together in Pt crucibles.
[2] Absorption in the IR: 90%; in the visible: 5%.
[3] Absorption in the IR: 83%; in the visible: 10%.

TABLE T 10–3. GENERAL SURVEY OF THE PROPERTIES OF TECHNICAL GLASSES[8]

The letters A to E determine groups of glasses according to the following rough arrangement:

A lead glasses (alkali lead silicates with 35—65 % $SiO_2 + Al_2O_3$)
B lime glasses (alkali lime silicates with 65—75 % $SiO_2 + Al_2O_3$)
C soft borosilicate glasses (alkali borosilicates with 70—85 % $SiO_2 + Al_2O_3$)
D hard low-alkali or alkali-free alumo-(boro)-silicates with 75—95 % $SiO_2 + Al_2O_3$[9]
E enamels

[10.2]

DENSITY	g/cm³	2.2 to 3.8[1]				
		A	B	C	D	E
Transformation point T_g	°C	360—420	430—500	430—540	600—800	150—600
Strain point $\eta = 10^{14.5}$ P (300—790 °C)[10]	°C	380—430	470—530	445—790		
Anneal point $\eta = 10^{13}$ P (350—890 °C)[10]	°C	425—460	500—570	480—890		
Softening point $\eta = 10^{7.6}$ P (440—1510 °C)[10]	°C	580—660	670—750	690—1510		
Mohs' hardness		4—8[2]				
Tensile strength[3]	kg/mm²	3—7	4—15	4—15	5—15	3—8
Compressive strength	kg/mm²	50—90	70—100	70—100	100	60—125
Bend strength	kg/mm²	10—25				
Torsional strength	kg/mm²	≈ 9				
Impact bend strength	cm kg/cm²	Average: 0.1 to 0.3				
Young's modulus	kg/mm²	Average: 5000—8000[4]				
Poisson's ratio	—	Usually 0.22—0.25; often less than 0.20				
Photoelastic constant	BREWSTER	Usually 2.6—3.3				
Thermal expansion coeff.[5]	$\frac{10^{-7}\ \text{mm}}{\text{mm °C}}$	85—95	80—110	30—60	8—38	70—120
Thermal shock resistance[11]	°C	50	60—115	150	(96 % SiO_2 :1000)	
Thermal stress resistance[12]	°C	17	19—30	50	(96 % SiO_2 :200)	
Thermal conductivity[6]	$\frac{10^{-3}\ \text{cal}}{\text{cm sec °C}}$	1.7—3.7	2.5—3.0	2.5—3.0	3	
Specific heat	cal/g °C	Limits (0—100 °C): 0.08—0.23[7]				
Transmission in the visible spectrum	%	For normal glasses (20 °C): 80—94				
Reflection R, absorption A, transmission D, of white light	%	Clear glass, 1—3 mm thick: $R = 8$; $A = 1$—3; $D = 90$—92				

TABLE T 10–3 *(continued)*

		A	B	C	D	E
Electrical resistivity[14]	Ω-cm	Limiting values (30 °C): 10^{11}—10^{17}				
		(10^{14})	(10^{12})	(10^{16})	(10^{17}—10^{18})	
$T_{\varkappa 100}$ point	°C	250—380	130—300	160—400	350—600	130—400
Dielectric constant[1]		Limiting values: 3.7—16.5				
		8.2	7.0	4.8		
Loss factor		Limiting values (10^3—10^6 c/s): 5—250×10^{-4}				
		Best soft-glass dielectrics (1.0 Mc/s): 5—10×10^{-4} Poor soft-glass dielectrics (1.0 Mc/s): 100—150×10^{-4}				
Electrical breakdown strength $d = 0.2$ mm[13]	kV/cm	20 °C / 3100	20 °C / 4500	20 °C / 4800		
		300 °C / 102	300 °C / 32	300 °C / 200		
$d = 1$ cm, 20 °C	kV/cm			50 c/s: 125 18 Mc/s: 11		

[10.2]

[1] The density is calculable from the composition (see GEHLHOFF). Pure B_2O_3-glass $\gamma = 1.812$; lithium borate $\gamma = 2.24$; heavy baryta and lead glasses (90% PbO) $\gamma = 7.21$. γ effectively determines the dielectric constant ($\varepsilon \approx 2.28\ \gamma$).

[2] Mohs' hardness for hard glasses: 7.5; for heavy Pb-glasses: 4.5; Knoop hardnesses: 324—570 kg/mm².

[3] Tensiles are strongly dependent on surface condition and shape of the glass; for the same types of glass, fibers 10 μ dia. go up to 180 kg/mm², whereas rods 50 mm dia. only to about 4 kg/mm² tear strength (see Fig. B 10-5).

[4] Young's modulus is low when there are internal strains, high with high B_2O_3 content (15% max.). It falls with rise in temp. (except in the case of pure quartz glass and borosilicate glasses with low thermal expansion coeffs.).

[5] That of strained glass is up to 2% higher.

[6] See also Fig. B 10-42; thermal conductivity rises with temp. (see Fig. B 10-43).

[7] Effect of temp. see Fig. B 10-43A, specific heat (17—100°) of Pyrex 0.2, of Sial 0.1975 cal/g.

[8] A purely qualitative comparison table; see Table T 11–6.

[9] See Chapter 11 (Quartz glass) for glasses with more than 95% SiO_2.

[10] Max. range.

[11] From CORNING; measured on glass plates $6 \times 6 \times {}^1/_4$ in. (see Chapter 10.2.V).

[12] From CORNING; for definition see Chapter 10.2.VI.

[13] From MOON; for 1 mm thickness limits 160—500 kV/cm.

[14] Cf. also Fig. B 10-44 ff.

TABLE T 10–4 (SUBDIVISION AS IN TABLE T 10–2) PROPERTIES OF THE

A. American glasses.

A1. Mfr.: CORNING GLASS WORKS, Corning, N.Y.

[10.2]

GLASS NO.	DESCRIPTION[32]	COLOR	MAIN USE	SOLD AS[1]	THERMAL EXPANSION COEFF. (0—300°C) [10^{-7}/°C]	MAX. WORKING TEMP. IN NORMAL OPERATION (°C)		THERMAL SHOCK RESISTANCE (°C)[2]		
						annealed	tempered	d = 3 mm	d = 6 mm	d = 12 mm
0010	Potash soda lead	None	Hot-filament lamps (tubes)	T	91[19]	110	—	65	50	35
0041	Potash soda lead	None	Thermometers	T	84	110	—	70	60	40
0050					91[18]					
0080	Soda lime	None	Lamp bulbs	BMT	92[18] [19]	110	220	65	50	35
0120	**Potash soda lead**	None	Foot glass for lamps and tubes	TM	89[19]	110	—	65	50	35
0240		None	CrFe seal		96[19]					
1710	Aluminosilicate	None	Cooking vessels	BP	42	200	400	135	115	75
1770	**Soda lime**	None	Universal	BP	82	110	220	70	60	40
1990	Low-loss iron sealing	None	Fe seal		127[19]	100		45	35	25
1991	Iron sealing	None	Fe seal		128					
2405	Hard Red	Red	Universal	BPU	43	200	—	135	115	75
2475	Soft Red	Red	Neon tubes	T	91	110	—	65	50	35
3320	Uranium[16]		W sealing		40[19]	200		145	110	80
3321	Hard Green Sealing	Green	W sealing	T	40	200	—	135	115	75
4407	Soft Green	Green	Pilot lamp	BPU	90	110	—	65	50	35
6720	**Opal**	White opal	Universal	P	80	110	220	70	60	40
6750	Opal	White opal	Illumination glass	BPR	87	110	220	65	50	35
6810	Opal	White opal	Illumination glass	BPR	69	120	240	85	70	45
7040	Borosilicate	None	Kovar seal	T	47[19]					
7050	Borosilicate (Clear sealing)	None	Sealing	T	46[19]	200	235	125	100	70
7052	**Borosilicate**	None	Kovar seal	BMPT	46 ± 1.5	200	210	125	100	70
7053	Low loss Kovar sealing				45					
7060	Kovar-sealing				50					
7070	**Borosilicate**	None	Elec. work (low tan δ)	BMPT	32[19]	230	230	180	150	100
7080	Soft low power loss				35					
7200	Quartz sealing				19					
7230	Quartz tungsten sealing				14					
7250	Borosilicate	None	Baking	P	36	260	260	160	130	90
				(1)				(2)		

CHIEF COMMERCIAL GLASSES USED IN VACUUM TECHNOLOGY

(data mostly from CORNING, [1]MONACK).

THERMAL STRESS RESISTANCE[3] [°C]	(4) STRAIN POINT (°C)	ANNEAL POINT (°C)	SOFTENING POINT (°C)	WORKING POINT (°C)	RELATIVE SURFACE HARDNESS[5]	DENSITY (g/cm³)	YOUNG'S MODULUS (kg/mm²)	$\log_{10}\varrho$ (ϱ = elec. res. [Ω-cm]) at T (°C): 25	250	350	DIELECTRIC PROPERTIES (20 °C, 10 Mc/s): $\tan\delta = 10^{-4}$ [33]	ε[33]	REFRACTIVE INDEX [n_D at 5893 Å]	OTHER PROPERTIES
19	397[13]	428	626[14]	970	—	2.85	6300	17[9]	8.9	7.0[20]	16[23] [24]	6.6[21] [22]	1.539	[26]
19	426	460	648	990	—	2.89	—	—	7.5	5.9	—	—	1.545	
	404	429	619			2.92			6.9	5.47			1.546	
17	478[13]	510	696[14]	1000	1.2	2.47	6850	12.4	6.4	5.1[20]	90[23] [24]	7.2[21] [22]	1.512	[26]
17	400	433	630	975	—	3.05	—	17[9]	10.1	8.0[20]	16[23]	6.6[21]	1.660	[26]
	397	425	607			2.97								
29	672	712	915[14]	1200	2.0	2.53	8900	17[9]	11.4	9.4	37[23]	6.3[21]	1.534	
19	470	503	710	—	—	2.40	—	—	—	—	27	6	1.496	
13	334	359	496	755		3.47	5900		10.1	7.7	4	8.3		
	366	393	539			3.18			9.6	7.3	4.5	8[22]		
36	506	537	770	1085	—	2.50	—	—	—	—	—	—	1.508	
17	466	501	693	1040	—	2.59	—	—	7.	6.2	—	—	1.511	
	497	535	780	1155		2.29			8.6	7.1	30	4.9	1.481	
39	497	535	780	1160	—	2.27	—	—	—	—	—	—	—	
17	485	518	695	—	—	2.53	—	—	—	—	—	—	1.525	
19	499	531	775	—	—	2.58	—	—	—	—	—	—	1.507	
18	445	475	672	—	—	2.63	—	—	—	—	—	—	1.513	
23	496	529	768	1010	—	2.65	—	—	—	—	—	—	1.508	
	450	484	702	1080		2.24			9.6	7.8[11]	50[8]	4.6[8]		[12]
34	461[13]	496	703	1025	—	2.25	—	16	8.8	7.2	33[24]	4.9[22]	1.479	[29]
34	438[13]	475	708	1115	—	2.28	—	17	9.2	7.4	26[23]	5.1 [21] [22]	1.484	
	502	535	727			2.73			13.5	11.3	6	6.1		
	463	495	690			2.23			8.5	6.9	33[23]	5.0	1.482	
70	455	490[14]	—	1100	4.1	2.13	4760	17[9]	11.2	9.1[20]	6[10] [23][24] [42]	4.0[21] [22][42]	1.469	
	413	450	726			2.15								
	583	645	1126											
	675	750	1160								11	3.85		
43	486	524	775	1190	3.2	2.24	—	15	8.2	6.7	28	4.7	1.475	
(3)	(4)				(5)									

[10.2]

TABLE T 10–4

A. American glasses.

A 1. Mfr.: CORNING GLASS WORKS, Corning, N.Y.

[10.2]

GLASS NO.	DESCRIPTION[32]	COLOR	MAIN USE	SOLD AS[1]	THERMAL EXPANSION COEFF. (0–300°C) [10^{-7}/°C]	MAX. WORKING TEMP. IN NORMAL OPERATION (°C)		THERMAL SHOCK RESISTANCE (°C)[2]		
						annealed	tempered	d = 3 mm	d = 6 mm	d = 12 mm
7340	Borosilicate	None	Manometers	T	67	120	240	85	70	45
7520	Borosilicate	None	Sealing		61					
7560	Borosilicate	None	Sealing		86					
7570	Solder glass	None	Solder glass (Al, mica)	Enamels	84[37]	100	—	—	—	—
7720	Lead-borosilicate (Nonex)[7]	None	Elec. work	BPT	36[19]	230	260	160	130	90
7740	Borosilicate (Pyrex)[7]	None	Universal	BPSTU	32[19]	230	260	180	150	100
7750	Borosilicate	None	Sealing		40[19]					
7760	Borosilicate	None	Sealing	BP	34	230	250	160	130	90
7780	Clear tungsten Sealing				37					
7900	96% Silica[17]	None	High temp.	BPTU	8	800	—	1250	1000	750
7900 (M)	96% Silica[17] (Multiform)	White opal	High temp.	M	8	—	—	—	—	—
7910	96% Silica[17]	None	UV transparent	BTU	8	800	—	1250	1000	750
7911	96% Silica[17]	None	UV transparent	T	8	800	—	1250	1000	750
7912	96% Silica[17]	None	UV transparent		8	800		1250	1000	750
7991	Tungsten sealing		W sealing		41	800				
8160	Dumet sealing		CrFe sealing		91	110		65	50	35
8830	Kovar sealing X-Ray				48					
8870	High lead	None	Sealing and elec. work	MTU	91	110	180	65	50	35
8871	Glass for dielectric purposes[34]				104	125		55	45	35
9010	Gray television				88.5					
9700	UV-Glass (Corex)	None	UV transparent	TU	37	220	—	150	120	80
9741	UV-Glass	None	UV transparent	BUT	39	200	—	150	120	80
9821	H. expans. UVT Special				93					
				(1)					(2)	

See Supplement to Table T 10–4 on pp. 648–649.

(continued)

(*data mostly from* CORNING, [1]MONACK).

THERMAL STRESS RESISTANCE[3] [°C]	(4) STRAIN POINT (°C)	ANNEAL POINT (°C)	SOFTENING POINT (°C)	WORKING POINT (°C)	RELATIVE SURFACE HARDNESS[5]	DENSITY (g/cm³)	YOUNG'S MODULUS (kg/mm²)	$\log_{10}\varrho$ (ϱ = elec. res. [Ω-cm]) at T(°C): 25	250	350	DIELECTRIC PROPERTIES (20 °C, 10 Mc/s) $\tan\delta = 10^{-4}$ [33]	ε[33]	REFRACTIVE INDEX [n_D at 5893 Å]	OTHER PROPERTIES
20	538	575	785	—	—	2.43	8000	16	8.5	6.9	—	—	1.506	
	530	566	747						6.8	5.5				
	503	536	702						6.6	5.4				
—	340[38]	365[38]	430[38]	560[38]	—	5.42	5650	—	10.64	8.66	22	15	—	
45	484	518	755	1110	3.2	2.35	6650	16	8.8	7.2	27[23]	4.7[21]	1.487	[26]
48	515[13]	555	820[14]	1220	3.1	2.23	6850	15	8.1	6.6[20]	46[23] [24]	4.6[21] [22]	1.474	[6] [26] [28] [29] [30] [31]
	431	467	704			2.19			9.5	7.7	24	4.3	1.474	
51	475	515	780	1210	—	2.23	6370	17	9.4	7.7	18	4.5	1.473	
	464	498	763			2.18			10.0	8.2				
200	820	910	1500[14]	—	3.5	2.18	6800	17[9]	9.7	8.1[20]	5[23]	3.8[21] [22]	1.458	
—	—	—	—	—	3.5	2.15	6800	17[9]	—	—	6	3.7	—	[25] [26] [27] UV transmission see Fig. B 11-8
200	820	910	1500	—	3.5	2.18	6800	17[9]	11.2	9.2	2.4[23]	3.8[21]	1.458	[25] [35] [27] UV transmission see Fig. B 11-8
200	820	910	1500	—	3.5	2.18	6800	17[9]	11.7	9.6	1.9[41]	3.8[41]	1.458	UV transmission see Fig. B 11-8
200	820	910	1500		3.5	2.18	6800							
	529	565	800	1180		2.34								
18	399	433	627	975		2.98			10.6	8.4	9	7.0	1.530	
	475	510	715			2.25			7.8	6.3	66	5.3		
22	398	429	580	—	0.6	4.28	5320	17[9]	11.8	9.7	9[23]	9.5	1.639	
15	357	384	527	770		3.84	580	18	11.1	8.8	5	8.45	1.65	[33] [34]
	411	442	650			2.59			8.9	7.0	22	6.5		
42	517	558	804	1195	—	2.26	—	15	8.0	6.5	—	—	1.478	[26] [27]
40	407	442	705	—	—	2.16	—	17[9]	9.4	7.6	—	—	—	[25] [26] [27]
	494	525	698			2.50			6.6	5.2				
(3)	(4)				(5)									

[10.2]

Footnotes to Table T 10-4 (A 1)

(1) Abbreviations:

B blown stock
M made in various forms
P pressware
S plate glass
R rolled sheet glass
T tubing and rod glass
U panels for CRTs and TV tubes

[10.2]

(2) Permissible temperature difference (°C) measured by quenching heated glass plates (150 × 150 mm) of given thickness d in cold water. Plates annealed, not tempered. For tempered parts, the thermal shock resistance may go up to double the values in the table.

(3) Temperature difference (°C) between the inner and outer surfaces of a glass tube or disk which gives at the cooler surface a tensile stress of 0.7 kg/mm² (= 1000 p.s.i.), calculated by the equation

$$S = \frac{\alpha E \Delta}{2(1-\mu)} .$$

S (kg/mm²)	tensile stress at cooler face, of thermal origin
Δ (°C)	interfacial temperature gradient
α (1/°C)	lin. thermal expansion coeff.
E (kg/mm²)	Young's modulus
μ	Poisson's ratio.

(4) These characteristic points correspond with the following values of viscosity:

strain point (lower stress relief temp.)	$\eta = 10^{14.6}$, recently $10^{14.5}$ poise
annealing point (upper stress relief temp.)	$\eta = 10^{13.4}$, recently $10^{13.0}$ poise
softening point	$\eta = 10^{7.6}$ poise
working point (operating temp. in flame)	$\eta = 10^{4}$ poise

(5) Relative values (standard soda-lime glass is set = 1) determined by subjecting the surface to sand blasting.

(6) Electrical breakdown strength, see Figs. B 10-77A and B 10-78.

(7) CORNING 7740 borosilicate glass is often known as "Pyrex", and 7720 as "Nonex". However, it must be pointed out that these terms are *general* trade-marks for about 150 different glasses, *not* names of *particular types of glass* (KOHL, HELDMANN). On the subject of Pyrex 7740, see also this table at the end of D 25.

(8) At 10^{10} c/s.

(9) Extrapolated.

(10) Measured at 10^{10} c/s: $\varepsilon \times \tan\delta = 80 \times 10^{-4}$.

(11) At 700 °C: 10^{3} Ω-cm.

(12) Compressive stress: $\sigma_{dB} = 49$ kg/mm²; bend stress: $\sigma_{dB} = 5.6$ kg/mm².

(13) See Fig. B 10-12.

(14) See Fig. B 10-15.

(15) For higher temps. and 10^{6} c/s see Figs. B 10-65 and B 10-70.

(16) Nonex-Pyrex joining glass.

(17) Details on these quartz-like glasses see Chapter 11.

(18) See Fig. B 10-26.

(19) See Fig. B 10-29.

(20) See Fig. B 10-49.

(21) See Fig. B 10-65.

(22) See Fig. B 10-67.

(23) See Fig. B 10-70.

24) See Fig. B 10-72.

Footnotes to Table T 10–4 (A 1) *(continued)*

(25) See Fig. B 10-94.
(26) See Fig. B 10-88.
(27) See Fig. B 10-95.
} UV transmission (cf. also Fig. B 11-8).

(28) See Fig. B 1-92 (IR transmission).

(29) See Fig. B 10-98 (alteration due to X-rays).

(30) See Fig. B 10-102 (attack by H_2O).

(31) See Fig. B 10-105A (attack by H_2O).

(32) Former descriptions see Supplementary Table I below. **[10.2]**

(33) ε and tan δ for various frequencies in the following Supplementary Table II.

(34) Obtainable also as flexible foil of even thickness (15—500 μ), width 6—150 mm.

(35) See Fig. B 10-240A and B (water release after various pretreatments and at different temps.).

(36) See Fig. B 10-259A.

(37) See Fig. B 10-259B.

(38) Max. working temp. 800°.

(40) Values in brackets are at 2.5×10^{10} c/s.

(41) See also Fig. B 11-7A.

(42) For higher temps. and 10^{10} c/s see also Fig. B 10-70B.

REF. (32): SUPPLEMENTARY TABLE I [from KOHL]

As the older trade names of CORNING glasses are often used even today and are found in the less recent literature, the corresponding designations are given together, to avoid mistaken belief on the reader's part that different types of glass are being treated.

FORMER LABORATORY CODE NO.	FORMER TRADE DESIGNATION	PRESENT TRADE DESIGNATION	FORMER LABORATORY CODE NO.	FORMER TRADE DESIGNATION	PRESENT TRADE DESIGNATION
G–1	001	0010	G–705–AO	706	7060
G–5	005	0050	G–707–DG	707	7070
G–8	008	0080	G–750–AJ	752	7520
G–164–HC	011	0110	G–805–F	753	7530
G–12	012	0120	G–805–G	755	7550
G–6 (obsolete)	013 obsolete	—	G–750–AL	756	7560
G–125–BB	024 (CrFe glass)	0240	G–71 (obsolete)	771 (obsolete)	—
G–189–IY	1990	1990	G–702–P ("Nonex")	772	7720
G–184–ET	1991	1991	G–726–MX ("Pyrex")	774	7740
G–371–BN	332 (Uranium glass)	3320	G–705–R	775	7750
G–705–BA	704	7040	GT–70	778	7780
G–705–AJ	705 (Clear sealing glass)	7050	G–704–EO	7991	7991
G–705–FN	7052 (Kovar glass)	7052	G–814–KW	816	8160
			G–858–V	887	8870

TABLE T 10–4 *(continued)* SUPPLEMENTARY TABLE II (see footnote [33])

Dielectric constant ε and dielectric loss factor $\tan\delta$ of the chief CORNING glasses at temperature T for various frequencies f (MASSACHUSETTS INST. OF TECHNOLOGY)

CORNING-GLASS NO.	TEMP. [°C]		ε AND $\tan\delta \times 10^4$ AT FREQUENCY f (c/s)								
			10^2	10^3	10^4	10^5	10^6	10^7	10^8	3×10^9	10^{10} c/s[40]
0010	24	ε	6.68	6.63	6.57	6.50	6.43	6.39	6.33	6.1	5.96
		$10^4\times\tan\delta$	77.5	53.5	35	23	16.5	15	23	60	90 (110)
[10.2] 0080	23[15]	ε	8.30	7.70	7.35	7.08	6.90	6.82	6.75	6.71	6.71
		$10^4\times\tan\delta$	780	400	220	140	100	85	90	126	170 (180)
0100	25[15]	ε	7.18	7.17	7.16	7.14	7.10	7.10	7.07	7.00	6.95
		$10^4\times\tan\delta$	24	16	13.5	13	14	17	24	44	63 (106)
0120	23[15]	ε	6.75	6.70	6.66	6.65	6.65	6.65	6.65	6.64	6.60
		$10^4\times\tan\delta$	46	30	20	14	12	13	18	41	63 (127)
1710	25[15]	ε	6.25	6.15	6.10	6.03	6.00	8.00	6.00	5.95	5.83
		$10^4\times\tan\delta$	49.5	42	33	26	27	34	38	56	84 (140)
1990	24	ε	8.40	8.38	8.35	8.32	8.30	8.25	8.20	7.99	7.94
		$10^4\times\tan\delta$	4	4	3	4	5	7	9	19.9	42 (112)
1991	24	ε	8.10	8.10	8.08	8.08	8.08	8.06	8.00	7.92	7.83
		$10^4\times\tan\delta$	12	9	6	5	5	7	12	38	51
3320	24	ε	5.00	4.93	4.88	4.82	4.79	4.78	4.77	4.74	4.72
		$10^4\times\tan\delta$	80	58	43	34	30	30	32	55	73 (120)
7040	25[15]	ε	4.84	4.82	4.79	4.77	4.73	4.70	4.68	4.67	4.64
		$10^4\times\tan\delta$	50	34	25.5	20.5	19	22	27	44	57 (73)
7050	25	ε	4.90	4.84	4.82	4.80	4.78	4.76	4.75	4.74	4.71
		$10^4\times\tan\delta$	93	56	43	33	27	28	35	52	61 (83)
7052	23[15]	ε	5.20	5.18	5.14	5.12	5.10	5.10	5.09	5.04	4.93
		$10^4\times\tan\delta$	68	49	34	26	24	28	34	58	81 (114)
7060	25	ε	5.02	4.97	4.92	4.86	4.84	4.84	4.84	4.82	4.80
		$10^4\times\tan\delta$	89	55	42	40	36	30	30	54	98 (90)
7070[42]	23	ε	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
		$10^4\times\tan\delta$	6	5	5	6	8	11	12	12	21 (31)
	100[15]	ε	4.17	4.16	4.15	4.14	4.13	4.10		4.00	4.00
		$10^4\times\tan\delta$	55	22	13	10	9	11		19	21
7720	34	ε	4.74	4.70	4.67	4.64	4.62	4.51			4.59
		$10^4\times\tan\delta$	78	42	29	22	20	23			43
7740	25	ε	4.80	4.73	4.70	4.60	4.55	4.52	4.52		4.52
		$10^4\times\tan\delta$	128	86	65	54	49	45	45		85 (96)
7750	25	ε	4.45	4.43	4.39	4.38	4.38	4.38		4.38	4.38
		$10^4\times\tan\delta$	45	33	24	20	18	19		43	54
7900	20	ε	3.85	3.85	3.85	3.85	3.85	3.85		3.84	3.82
		$10^4\times\tan\delta$	6	6	6	6	6	6		6.8	9.4 (13)
	100[15]	ε	3.85	3.85	3.85	3.85	3.85	3.85		3.84	3.82
		$10^4\times\tan\delta$	37	17	12	10	8.5	7.5		10	13
For comparison:											
Fused quartz Quartz glass	25[15]	ε	3.78	3.78	3.78	3.78	3.78	3.78	3.78	3.78	3.78
		$10^4\times\tan\delta$	8.5	7.5	6	4	2	1	1	0.6	1 (2.5)

Footnotes see pp. 32–33.

A 2. Various American laboratory glasses

NO.	DESCRIPTION	α 20—300 °C [10^{-7}/°C]	T_g [°C]	EXPANSION CHARACTERISTIC	NOTES
286	CrFe sealing	101	*ca.* 380	see Fig. B 10-30	from HULL
430–Ti	CrFe-stainless steel ("430–Ti") sealing glass	100	(3)		
542	Fe sealing(1) (2)	113	*ca.* 350	see Fig. B 10-30	from HULL
1075	FeNi 42 sealing	51	*ca.* 410		
Low-loss glass, see HOOD(1)		—	—	—	tan δ = 4.2×10^{-2}
Low-loss glass, see ARMISTEAD(1)		128	Softening temp.: 588		tan δ = 4.5×10^{-4}, ε = 8.1
542x	Fe sealing(1) (4)	125	380—400	—	tan $\delta = 10^{-3}$

[10.2]

(1) Composition see Table T 10–2, A 2.
(2) Further data, from [6]STEVELS unless otherwise stated:
$T_{str} = 385$; $T_{an} = 400$; $T_{soft} = 560$; $T(\eta = 10^{12}$ poise$) = 450$ ([5]STANWORTH)
$\varepsilon = 7.7$; tan δ (20 °C, 10 Mc/s) $= 8.3\times10^{-4}$; tan δ (20 °C, 400 Mc/s) $= 18\times10^{-4}$
ϱ (20 °C) $= 2.5\times10^{17}$; ϱ (120 °C) $= 10^{14}$; ϱ (200 °C) $= 3\times10^{11}$ Ω-cm;
$T_{\times100} = 320$ °C (from [2]KRATOCHVÍL).
(3) $T_{str} = 438$; $T_{an} = 470$ (see HAGY). (4) Mfr. unknown, similar to 542 glass.

A 3. American hard glasses for X-ray tube envelopes (ZUNICK)(2)

NO.	MFR.	α [10^{-7}/°C]	STRAIN POINT [°C]	ANNEAL POINT [°C]	SOFTENING POINT [°C]	log ϱ (ϱ in Ω-cm) 250 °C	350 °C	BREAKDOWN STR. (kV/cm) 25 °C	200 °C
L 650(3) (4)	LIBBEY-OWENS	47	473	503	711	7.99(1)	6.35	140	32
866 LC(5)	CORNING	48	483	513	716	7.68	6.24	n.g.	61
402(4)	MCKEE	45	452	493	734	7.90	6.45	n.g.	84

(1) See also Fig. B 10-56A.
(2) With reduced elec. insulation properties to avoid wall charges.
(3) Analysis see Table T 10–2, A 3. Re coloring due to X-ray beams, see Fig. B 10-98.
(4) Also for Kovar caps and ring seals (see e.g. BLACK).
(5) See also CORNING X-ray glass 8830 in Table T 10–4, A 1.

A 4. American glasses for TV tube envelopes

NO.	DESIGNATION	NOTES
5533	Pittsburgh Teleglass	Can be directly sealed to stainless steel 430 (see Table T 6.1–12, group C); glass absorbs X-rays with only gradual discoloration and has a light grey tint to improve picture contrast; light transmission is 77%

A 5. LIBBEY GLASS DIV., OWENS ILLINOIS GLASS CO.
A 6. KIMBLE INDUSTRIAL GLASSES, OWENS ILLINOIS GLASS CO.
See pp. 650 and 651.

DESIGNATION	MFR.[2]	γ [g/cm³]	α 20–300 °C [10⁻⁷/°C]	T_g[11] [°C]	M_g [°C]	$T_{\chi 100}$ [°C]
AH[1]	Po	2.47	89[10]	510	540	
BO tyčinky	Po	2.59	63		(580)	
BO tyčinky měkké	Po	2.52	103		(540)	
C glass[1] [6]	Ka		50	630	675	
D 47[1]	Ka	(2.46—2.50) 2.48	87 ± 2[10]	530 ± 2%	560	200—212
E glass[1] [6]	Ka		54	695	730	
Enamel	Po	3.45	89		(520)	
F 46[1]	Ka	—	95[10]	525	555	
Fe glass	(Sv)	3.16	125	385	430	315—325
FeCr glass	Ka	3.25	100	415	460	330
Kovar, formerly K 705[1]	Ka	(2.18—2.30)[12] 2.22	47 ± 2	460—470	540	350 (310)[16]
LL low-loss glass, formerly K 707[1]	Ka	(2.12—2.20) 2.16	32 ± 2[10]	480	575	410[16] 430
KS[1] [6]	Ka	2.49	87	520	570	159
M glass[1], Pb glass	Po	(2.9—3.14)[12] 3.01	94 ± 2%[10]	465	465[3]	(≧ 325)[7] 343
Molybdenum MoKa[1]	Ka	(2.28—2.36)[14] 2.32	50 ± 2[10]	550	605	200—230
Neon glass	Po					
O-Svor	Sv	2.9—3.14	92[10]	[4]	445	≈ 330[7] 355[16]
P 31[1]	Po	2.37	52	560	620	—
Palex[1] [6]	Ka	2.45	64	540	590	203
Pb-Nižbor	Ni		86[10]	410—430	(455–478)	
PN[1]	Po	2.58	80 ± 2[10]	530 ± 15	(580)	210 (170)[16]
Sial[1]	Ka	2.39	47	540	590[5]	205
Simax[14]	Ka	2.25	27.5—31.5	490 ± 20	590[13]	250
Unihost[1]	Ho	2.49	94	490[8]	530	160
Wolfram WoKa[1]	Ka	(2.28—2.36)[12] 2.32	40 ± 2[10]	485	575	330
Žárovkové sklo (electric bulb glass)	Ko	(2.46—2.59) 2.52	98 ± 2	462 ± 2%	545[15]	(150—170)

[10.2]

(1) Data from VÚ SKLÁŘSKÝ, $T_{\chi 100}$ partly also from [2]ONDRÁČEK.
(2) Mfr.: explanation of abbreviations see Table T 10–2, footnote 50.
(3) T_{str} = 385° (360°[7]); T_{an} = 415° (390°[7]); T_{soft} = 593° (590°[7]); T_{work} = 950° (900°[7]).
(4) T_{str} = 385°; T_{an} = 408°; T_{soft} = 610°; T_{work} = 935°.
(5) T_{soft} = 815°.
(6) Usable in vacuum technique, but not proved in glass-metal sealing.
(7) From [2]KRATOCHVÍL. (8) From [2]KRATOCHVÍL: T_{str} = 470°; T_{an} = 505°.

ommercial glasses (suppl. from [5]VOLF)

THERMAL SHOCK RESISTANCE ΔT [°C]	HYDROLYTIC CLASSIFICATION	SOLUBILITY[9] [DGG] mg	tan $\delta \times 10^{-4}$ [10 Mc/s, 20°C]	NOTES E = Young's modulus (kg/mm²); σ_{zB} = tensile str. (kg/mm²); ε = dielectric constant
130	III		—	Soft apparatus-glass
	I			
180	I	9		Low-alkali glass for fiber braid mfr.
146	II—III	16		Sealing glass for FeNi 50/50; $\alpha = 86\text{–}92 \times 10^{-7}$ 1/°C and inflexion point at 475°; mouse-gray color seal
180	I	12	—	Low alkali braid fiber glass
120	III	(25—30)		Soft apparatus-glass
80			(10) 8	Fe sealing glass
(58)	(III)	(25—50)	14	Fe (ferritic) sealing glass
250	V	150 ($\leqq$ 190)	35	Kovar sealing; gray seal color; $\varepsilon = 5.1$
316	IV	48—80	($<$ 10) 7	Vey low dielectric loss; seal color, chocolate brown
100—120 (140)	II	17—23	76	Technical apparatus; $E = 7300$; $\sigma_{zB} = 7.5$
(106)	II	(15—25)	($\leqq$ 25) 15	Pb glass for Dumet sealing
230	I	5.5	70	Mo sealing; chocolate seal-color; $\varepsilon = 6.9$
				Neon illumination tubes
	II			Pb glass for Dumet sealing
210	I	—	—	Chemically resistant glass
170	I	9	63	Press glass
				Pb glass for Dumet sealing
150	II—III	(15—25)	100	Thermometer glass
220—240	I	5.5	70	Hard apparatus glass; $\varepsilon = 6.9$; $\vartheta = 3.2_2$ Brewster $E = 7500$; $\sigma_{zB} = 14.6$
355 $\pm$ 20	I	3—5	40	Hard apparatus glass; $\varepsilon = 4.01$; $E = 6900$
105	III		100	Apparatus glass
(250)	I	7	35	W sealing glass (red-brown seal color); $\varepsilon = 4.7$
(102)	IV	(25—50)	87	Hot-filament lamp bulbs, annealing range 390—500° $\pm$ 10°

[10.2]

[9] Test method as per DGG; see Section 10.2.XX.
[10] See also Fig. B 10-35.
[11] Transformation point T_g defined here as T for viscosity = $10^{13.47}$ poise.
[12] Limits.
[13] $T_{soft} = 760°$ ($\eta = 10^{7.6}$ poise).
[14] From [5]VOLF.
[15] $T_{soft} = 600° \pm 2\%$; $T_{work} = 1040° \pm 3\%$. [16] From [2]ONDRÁČEK.

TABLE T 10–4 *(continued)* *D. German commercial glasses*

I. Pre-war mfr. and present-day mfr. in Western Germany

D 1. Mfr.: ALT, EBERHARD UND JÄGER, *Ilmenau (pre-war mfr.)*

(a) Earlier types

DESIGNATION	α 20–100 °C [10^{-7}/°C]	α 20–300 °C [10^{-7}/°C]	T_g [°C]	NOTES
A hard glass	70		540	Alumo-borosilicate
[10.2] Pb glass 500	80	86	410	49% PbO content
Pb glass BG	85	94	420	
FK	86		430	Alumo-lime silicate; for neon tubes Hg-resistant
L 1 Fe sealing				Alkali alkaline-earth silicate
Standard thermometer glass	79	86	415	Alkali alkaline-earth silicate
Opal (3 layer) glass	88		450	Fluoro-lime-zinc silicate

(b) Modern special technical glasses

DESIGNATION	γ [g/cm³]	α 0–200 °C [10^{-7}/°C]	α 0–400 °C [10^{-7}/°C]	T_g [°C]	SOFTENING POINT [C°]	$\tan\delta \times 10^{-4}$	HYDR. CLASS.	NOTES
A glass (see also Table T 10–4, D 20)	2.54	63	65	545	760	57	I	Apparatus glass
E glass	2.62	94	98	512	550	52	III	Sealing; Al-CaO-silicate
M glass	3.10	100	106	437	480	10	III	Pb glass
N glass (see also Table T 10–4, D 20)	2.58	79	86	530	690	73	III	Standard; Al-CaO-silicate
R glass	2.48	105	109	493	543	—	IV	Apparatus glass

DESIGNATION	γ [g/cm]³	α (20–300°) [10^{-7}/°C]	T_g [C°]	SOFTENING TEMP.(1) [°C]	$T_{\chi 100}$ [°C]	NOTES ε = dielectric constant $\tan\delta$ = loss angle d = breakdown strength (kV/mm)
D 2. Mfr.: DEUTSCHE SPIEGELGLAS-GESELLSCHAFT						
R 51		81	437		410	$\varepsilon = 8—9$; $\tan\delta = 5—6 \times 10^{-4}$
D 3. Mfr.: GLASWERK G. FISCHER, *Ilmenau i. Thüringen; pre-war mfr.*						
357 special chemical glass		67	544	593	212	For FeNi 46 and ceramics of the Frequenta, Kerafar, Ergan and Calit types. Chemical apparatus glass of hydrolytic classification I

DESIGNATION	γ [g/cm³]	α (20–300°) [10⁻⁷/°C]	T_g [°C]	SOFTENING TEMP.(1) [°C]	$T_{\eta 100}$ [°C]	NOTES ε = dielectric constant tan δ = loss angle d = elec. breakdown strength (kV/mm)
827 UV glass		92	502	544	209	Transparent for 2700—4000 Å
1140 UV dark filter glass		89	498	538	—	Transparent for 2800—4000 Å, absorbs in the visible
1238 Fe sealing		126(2)	474	500	121	For pure and Armco Fe
Ampullax		85(2)	556	596	251	For FeNi 50, fired natural steatite and ceramic "T 2" [10.2]
Gege-Eff standard thermometer glass (cf. also D 17)		84(2)	(530—) 536	581	144	Sealing glass for FeNi 50; tan $\delta > 40 \times 10^{-4}$
Lumophor glass		(0–100) 89		470		Fluorescent glass
M glass (steatite sealing)		75(2)	530		—	
Mo sealing glass		50(2)	487	553	216(3)	For Mo and Kovar II and hard porcelain Melalith
Pt sealing glass		92(2)	526	585	245	
Prima glass (cf. also D 17)	2.45	92	518 (—530)	575	220	Hydrolytic classification III; tan $\delta > 35 \times 10^{-4}$; for Dumet wire and ferr. CrFe
Prima A glass		99	507	547	183	Type: "Thüringer glass"
Röntgen glass		102	491	540	212	For knife-edge Cu ring (Housekeeper) seals and ferr. CrFe
X glass		103.5	502	540	190	

(1) Measured on a glass rod, l = 100 mm, dia. = 4—5 mm, in dilatometer (spring pressure).
(2) See also Fig. B 10-36. (3) See also Fig. B 10-52.

D 6. Mfr.: E. GUNDELACH, *Gehlberg i. Thüringen, pre-war mfr.*

DESIGNATION	γ [g/cm³]	α [10⁻⁷/°C]	T_g [°C]	SOFTENING TEMP. [°C]	$T_{\eta 100}$ [°C]	NOTES
Apparatus glass	2.58	(25—75 °C) 88(1)	515	650	(220—) 270	see also Osramglass 584 d
Platinum glass		(20—300 °C) 90				

(1) See also Fig. B 10-36.

D 7. Mfr.: PUTZLER, *pre-war mfr.*

DESIGNATION		α (20-100 °C) [10⁻⁷/°C]				
Resisto		54				

TABLE T 10–4 *(continued)* *D 8. Mfr.:* OSRAM KOMM.-GES. *(pre-war at Weisswasser,*

	DESIGNATION	γ [g/cm³]	α 25–75°C [10^{-7}/°C]	TWB[1] [°C]	T_g [°C]	TEMPERATURE FOR 10^{12} P [°C]	TEMPERATURE FOR 10^{11} P [°C]
	105 Magnesia glass	2.51	89[3]	99	508	530	555
[10.2]	110 Resisto glass	2.40	49	179	510	557	586
	122 p Thüringer apparatus glass, Hg-resistant	2.47	94	101	500	535	561
	123 a high-lead M glass (31% PbO)	3.11	86[3] (0—400 °C) (91)	92	425	453	482
	140 white opal glass	2.56	89	—	525	564	591
	172 a T glass (Pb-free Thüringer glass)	2.54	96	92	495	536	565
	301 b Pt sealing high-lead	3.28	89 (20—300 °C) (95)	84	445	483	511
	352 Pb glass (22% PbO) tube glass	2.84	91	97	420 (436)	450	479
	362 a W sealing glass, contains Pb	2.35	39[3]	220	522 (536)	559	584
	394 b hard glass for high-temperature use	2.24	33	238	560 (522)	—	—
	424 d chemically resistant apparatus glass	2.39	51	169	580	608	636
	550 UV soft glass (bulbs)	2.49	88	93	510	—	—
	562m ceramic sealing glass	2.43	55[3]	136	567	—	—
	584 d medium-hard Thüringer apparatus glass	2.64	88[3]	89	530	552	578
	594 UV soft glass	2.49	88	93	510		
	612 i Na-resistant glass	—	55	—	515	—	—
	630 f IR absorption glass	2.59	68	—	533	563	587
	637 h Mo sealing glass	2.38	48[3]	171	550	598	628

*ıow Augsburg) (*OSRAM *data, unless otherwise stated)*

VISCOSITY η		$T_{\chi 100}$	DIELECTRIC DATA FOR 10^9 c/s			NOTES
10^{10} P	10^9P		ε	tan $\delta \times 10^4$		
°C]	[°C]	[°C]	[20 °C]	[20 °C]	[350 °C]	
586	627[5]	173	—	—	—	For standard clear-glass bulbs
617	657	280	—	—	—	For internal construction of high-wattage hot-filament lamps [10.2]
593	631	220	6.4	36	120	For neon and Hg low-pressure lamps, colorless
515	559[5]	325[4]	6.0	80—90	200—220	High insulation resistant tube glass, suitable for ferr. CrFe and Dumet wire
621	657	180	—	—	—	Hot-filament lamp bulbs
600	641	270	6.6	31	60	Hot-filament lamp parts
543	583[5]	365	7.9	20	50	Specially highly insulating
514	552	270 (288)	—	—	—	For Dumet wire, good insulating properties
618	664[5]	356[4] (328)	4.4	45	135	Highly insulating, for high-wattage lamps
—	—	230	6.5	41	120	Suitable for welding (see 10.3. V)
671	727	200	5.4	56	160	Can be sealed to Ag (HUNT), for X-ray tubes, for $M^{\cdot} < 1$ mm dia. (KNAPP)
—	—	188	—	—	—	Colorless; $D = f(\lambda)$ see Fig. B 10-89
—	—	240	—	—	—	
609	646	247	6.6	30	70	For high-wattage hot-filament lamps and TV tubes
		185	—	—	—	Pale-blue for hot-filament lamps $D = f(\lambda)$ see Fig. B 10-89
—	—	—	—	—	—	For Na-vapor lamps
616	651	—	—	—	—	Absorbs in the IR
662	702[5]	245	—	—	—	Good insulator for transmitter, rectifier, and TV tubes

TABLE T 10–4 *(continued)* *D 8. Mfr.:* OSRAM KOMM.-GES. *(pre-war at Weisswasser,*

DESIGNATION	γ [g/cm³]	α 25—75 °C [10^{-7}/°C]	TWB(1) [°C]	T_g [°C]	TEMPERATURE FOI 10^{12} P [°C]	10^{11} P [°C]
637n Mo sealing glass	2.36	49	167	570	605	635
[10.2] 637x Mo sealing glass of very high insulation resistance	2.36	47	183	570	—	—
640a UR black glass	2.63	88	—	515	—	—
712b W sealing glass, Pb-free	2.28	42(3)	192	565	597	635
712h UV hard glass, Pb-free	2.28	42	192	565	597	635
742 high softening point hard glass for hot-filament lamps	2.62	31 (20—300 °C) (35)	171	735	781	813
743g Pb-free Dumet sealing glass	2.71	91	—	460	498	528
753 UV black glass, soft	2.60	89	—	512	—	—
756b Fernico sealing, contains Pb	2.24	49 (20—300 °C) (51)	172	500	528	556
779a apparatus glass	2.53	68	103	550	—	—
835a UV glass, resists Hg	2.58	90	—	510	553	579
906c Mo sealing glass		≈ 48		≈ 490	—	—
911b Fernico sealing glass, Pb-free		≈ 47		≈ 500	—	—
Z 24 intermediate glass		24		≈ 603	—	—
Z 28 intermediate glass		28		≈ 558	—	—
Z 54 intermediate glass		54		≈ 530	—	—
Z 63 intermediate glass		63		≈ 530	—	—
Z 70 intermediate glass		70(3)		≈ 530	—	—
Z 78 intermediate glass		78		≈ 530	—	—

(1) In accordance with Standard DIN 52 325 (thermal shock resistance).
(2) From [2]THOMAS.

now Augsburg) (OSRAM data, unless otherwise stated) (continued)

VISCOSITY η		$T_{\chi 100}$	DIELECTRIC DATA FOR 10^9 c/s			NOTES
			ε	$\tan\delta \times 10^4$		
10^{10} P [°C]	10^9 P [°C]	[°C]	[20 °C]	[20 °C]	[350 °C]	
672	719	295	5.1	42	80	For internal parts, very good insulation properties
—	—	338	—	> 50	—	For internal parts of high power tubes
—	—	205	—	—	—	IR-transparent
681	738	343	4.8	45	120	High insulation properties for high-wattage hot-filament lamps; for W
681	738	343	—	—	—	For W sealing; UV transmission, see Fig. B 10-89 and KOPEC
850	896[5]	450	6.1	40	120	For very high power hot-filament lamps
561	604	274	—	—	—	For Dumet wire seals
—	—	207	—	—	—	$D = f(\lambda)$, see Fig. B 10-89
589	637	222	5.1	50	150	For Kovar and Fernico
—	—	204	6.6	38	80	
611	650	250	—	—	—	For Hg low-pressure lamps $D = f(\lambda)$, see Fig. B 10-89
—	—	≈ 290	—	—	—	Contains Pb and B_2O_3; good insulator
—	—	≈ 340	5.3	77	—	Good insulator
—	—	—	—	—	—	Intermediate glasses
—	—	—	—	—	—	
—	—	225	—	—	—	
—	—	183	—	—		
—	—	188	—	—	—	
—	—	205	—	—	—	

[10.2]

[3] See also Fig. B 10-37.
[4] See also Fig. B 10-52.
[5] See also Fig. B 10-19.

1	2	3		4	5	6	7	8	9	10
DESIGNATION	γ	α [10^{-7}/ °C]		T_g	T_{str}	T_{an}	T_{soft}	T_{work}	TWB	E
	g/cm³	20—100 °C	20—300 °C	[°C]	[°C]	[°C]	[°C]	[°C]	[°C]	[kg/mm²]
16 standard glass	2.58	82	90	535	495	537	712	1000	110	7370
1447 Mo glass	2.48	50	51	520	483	529	725	1080	185	6870
[10.2] 1639 Mo sealing glass	2.30	49	50	525	501	540	736	1025	180	—
1646 W glass	2.27	41	42	510	485	534	754	1095	190	6750
2877 (similar to apparatus glass 20)	2.39	48	49	555	524	569	794	1190	200	7240
2954 thermometer glass	2.42	60	64	586	548	590	780	1125	140	7350
2955 W glass "Supremax"	2.47	33	37	710	665	715	938	1220	205	8790
Fiolax brown glass	2.46	54	55	546	517	560	773	1140	170	7060
W glass "Suprax"	2.31	39	39	545	516	567	793	1195	215	6640
4210 Fe glass	2.68	116	127	440	415	455	614	880	—	—
8095 Pb glass	3.02	92	99	425	385	430	595	950	—	—
8196 TV tube glass	2.59	91	98	430	402	440	660	1025	110	6630
8212 W glass	2.31	40	41	485	470	520	742	1138	200	6440
8243 Kovar glass	2.26	50	52	480	455	497	715	1040	185	6060
8330 Duran 50 (W glass)	2.23	32	32	520	510	568	815	1245	250	6290
8401 Mo Uviol glass		(52)		(598)						
8405 Uviol glass	2.51	94	99	435	391	446	657	985	—	—
8407 pharmaceutical bottle glass	2.50	76	80	543	505	547	732	1045	120	7530
8412 Fiolax clear glass	2.39	48	49	552	519	565	783	1165	195	—
Glass solders										
8435 Li and PbO alumoborosilicate glass	2.30	—	58	412	—	—	549	—	—	—
8461 lead-borate glass + SiO_2	5.19	—	83	403	—	—	485	—	—	—
8468 lead-borate glass + ZnO	6.87	—	20–200 °C 124	265	—	—	330	—	—	—

11	12	13		14	15	16			17
λ $\left[\frac{10^{-3}\ \text{cal}}{\text{cm s °C}}\right]$	$T_{\varkappa 100}$ [°C]	$\log_{10}\varrho = A + B/T$		ε [10^6 c/s]	$10^4 \tan\delta$ [10^6 c/s]	CHEMICAL CLASSIFICATION			NOTES, APPLICATIONS
		A	B			HYDR.	ACID	AL-KALI	
2.44	165	—2.19	4.46	6.37	60	III	I	II	Thermometers, for Pt up to 1 mm dia., and steatite
2.51	197	—1.80	4.60	5.00	67	I	I	III	For Mo and Kovar up to 3 mm dia.
—	232	—1.72	4.89	—	—	IV	II	III	For Mo any thickness, and Kovar caps
—	252	—1.61	5.05	4.16	23	III	II	III	For W in general; intermediate glass for W and Duran 8330
2.83	195	—1.44	4.41	4.94	51	I	I	II	For Mo $\ll$ 1 mm dia.
—	137	—1.47	3.89	—	—	I	I	II	For ceramic "Frequenta" and FeNiCo $\ll$ 3 mm dia.
2.83	517	+0.33	6.06	5.01	17	I	(IV)	III	For W up to 1 mm dia.
2.68	—	—	—	—	—	I	I	II	Ampoule glass
2.72	245	—1.51	4.93	4.52	50	I	I	II	For W $\ll$ 3 mm dia.
2.24	177	—2.48	4.71	6.53	20	(V)	(IV)	III	For Fe sealing
—	326	—2.77	6.45	—	—	III	III	III	For glass foot
—	272	—4.5	6.78	5.60	28	III	I	II	TV tube envelopes
2.60	401	—1.16	6.17	5.48	79	II	I	III	For W up to 4 mm dia.
2.50	342	—1.92	6.10	4.40[2]	18[2]	(V)	(V)	(IV)	For Kovar, etc., and Mo
2.79	248	—1.44	4.91	4.20	44	I	I	II	For W up to 1 mm dia. Mo, FeNiCo, up to 3 mm dia.
—	268	—3.12	6.02	—	—	IV	I	II	UV-transparent
—	—	—	—	—	—	I	I	II	Ampoules
—	—	—	—	—	—	I	I	II	Ampoules
—	351	—	—	—	—	—	—	—	
—	394	—	—	—	—	—	—	—	
—	255	—	—	—	—	—	—	—	High Pb-content

[10.2]

Footnotes to Table T 10–4, D 9:

(1) Explanation of abbreviations:

Col. 2: γ = density.
Col. 3: α = average linear expansion coeff.
Col. 4: T_g = transformation temp.
Col. 5: T_{str} = viscosity $\eta = 10^{14.5}$ P.
Col. 6: T_{an} = viscosity $\eta = 10^{13.0}$ P.
Col. 7: T_{soft} = viscosity $\eta = 10^{7.6}$ P.
[10.2] Col. 8: T_{work} = viscosity $\eta = 10^{4.0}$ P.
Col. 9: TWB = thermal shock resistance as per DIN 52 325.
Col. 10: E = Young's modulus.
Col. 11: λ = thermal conductivity.
Col. 12: $T_{\varkappa 100}$ = temp. for 10^8 Ω-cm.
Col. 13: A and B = constants in the RASCH-HINRICHSEN equation; ϱ (Ω-cm) = elec. resistivity, T (°K) = temperature.
Col. 14: ε = dielectric constant at 1 M c/s
Col. 15: tan δ = dielectric loss angle (units of 10^{-4}) at 1 M c/s.

(2) Note added in proof: recent values, esp. of tan δ at 10^9 c/s, are given by BLUME, H. AND A. HINCKELDY: *Siemens-Z. 33* (1959) 724.

TABLE T 10–4 *(continued) D 11. Mfr.:* SENDLINGER OPTISCHE GLASWERKE *(post-war mfr., 1954)*

CODE	AVERAGE EXPANSION COEFF. [10^{-7}/°C](4)					T_g(1)	M_g	$T_{\varkappa 100}$	NOTES
	20 to 100 °C	20 to 200 °C	20 to 300 °C	20 to 400 °C	20 to 500 °C	[°C]	[°C]	[°C]	
96/2	46	47	48	48	—	470 (475)(3)	535	287	Fernico sealing glass
V 130 i	96	102	105	108	113	520 (470)(3)	556	179	For cap seals with Cu or Fe(2)
V 312	90	94	97	100	104	520 (470)(3)	567	183	Sealing glass for ferr. CrFe(2)
V 315 M	49	51	51	52	59	490 (510)(3)	570	197	Mo sealing glass
V 320 w	49	51	53	55	57	515 (545)(3)	610	294	Sealing glass for special ceramics; also with special precautions, can be used for W sealing

(1) Determined from the inflexion point in the expansion curve in Fig. B 10-39.

(2) Does not discolor under exposure to X-rays.

(3) A temperature value given in the mfr.'s catalogue as "stress relief temperature", without the latter term being defined.

(4) See also Fig. B 10-39 for expansion characteristics.

TABLE T 10–4 *(continued) D 12. Mfr.:* SOPHIENHÜTTE, *Ilmenau. Pre-war mfr., see also D 24*

CODE	α (20—100 °C) [10^{-7}/°C]	T_g [°C]	SOFTENING POINT [°C]
3	87	—	≈ 575
9	78	—	≈ 580
17	56	—	≈ 610
20	73	—	≈ 590
171	91	—	≈ 575
S I Neutral	51	615	—

[10.2]

D 13. Mfr.: RUHRGLAS, *Essen*

DESIGNATION	α [10^{-7}/°C]			T_g	M_g[1]	T_{soft}[2]	CLASSIFICATION[3]		
	20 to 200 °C	20 to 300 °C	20 to 400 °C	[°C]	[°C]	[°C]	HYDROL.	ACID	ALKALI
AR[7]	91	95	99	≈ 520 542[4]	≈ 566 584[5]	≈ 716 708[6]	III	I	II
ARN	78	80	83	525	582	728	II	I	II
LR brown	105	109	113	492	534	671	(V)	II	II
LR white	107	110	114	479	534	669	(V)	II	II
MGR	101	104	109	484	532	671	IV	I	II

(1) M_g = deformation temp. ($\eta = 10^{11}$ P approx.); cf. Table T 10–5.

(2) $\eta = 10^{7.65}$ P; see Table T 10–5.

(3) See Tables T 10–15, T 10–17, T 10–16.

(4) From measurements by the VEB Central Laboratory, Ilmenau/Thüringen.

(5) For $\eta = 10^{12}$ P.

(6) For $\eta = 10^{8}$ P.

(7) $T_{\varkappa 100} = 211°$.

TABLE T 10–4 *(continued)* *D 14.* GLASWERK-WERTHEIM, *Wertheim a. Main*

DESIGNATION	AVERAGE LINEAR EXPANSION COEFF. 10^{-6}/°C			T_g	M_g	$T_{\eta 100}$	HYDROL. CLASSIFICATION	NOTES BASED ON FIRM'S DATA
	20–100°C	20–400°C	20 T_g°C	[°C]	[°C]	[°C]		
AW tube glass	87	95	97	525	580	220	III	Machine-drawn clear tubing for neon-filled devices, glass apparatus
EW sealing glass contains Pb	42	44	45	505	565	320	I	Electrotechnical glass apparatus also Mo sealing, Kovar, Fernico, ZB (steatite); speciality for liquid IIe storage vessels
FW luminous tube glass	88	97	98	500	550	240	III	Colored and fluoresc. tube, for making neon lighting
GW apparatus glass	87	95	97	525	580	205	III	Chemical hollow-ware, tube, capillary tubing, sealing glass for ferr. CrFe (e. g. "Vacovit 025") FeNi (≈ 50/50), e. g. "Vacovit 501" and "511", steatite Gl. 9
LW Pb-free glass	88	97	100	520	570	250	III	Electrotechnical glass apparatus sealing glass for ferr. CrFe (e. g. "Vacovit 025"), FeNiCr 52/42/6, e. g. "Vacovit 426", FeNi (≈ 50/50), e. g. "Vacovit 511"
LX Röntgen glass	88	97	100	520	570	250	III	Unworked tube for X-ray tubes, seal glass for ferr. CrFe, FeNiCr 52/42/6 ("Vacovit 426"), FeNi ≈ 50/50, ("Vacovit 511")
MW (leaded) sealing glass	89	99	102	420	460	280	III	Seal glass for Pt, Platinite, Dumet, FeNiCr (52/42/6) ("Vacovit 426") electrodes
NW standard thermometer glass	80	89	90	540	600	165	III	For use up to 460°, densimeters pyknometers, seal glass for Pt, FeNi (≈ 50/50) ("Vacovit 501"), steatite Gl.
R apparatus glass	57	63	64	570	620	255	I	Chemical hollow-ware for temp. resistance, seal glass for FeNiCo, esp. "Vacon 10", "12", "20", and for Frequenta 221 (steatite)
S sterilizable glass	72	81	84	530	590	210	II	Easily sterilized apparatus, ampoules, water-gauge tubes

TABLE T 10–4 *(continued)* *D 15. Mfr.: Various firms*

DESIGNATION	MFR.	α 20—100 °C [10^{-7}/°C]	T_g [°C]	SOFTENING POINT [°C]	NOTES
Phosphate glass	(I.G. FARBEN?)	88		560	
	For supplementary data:				

[10.2]

TABLE T 10–4 *(continued)* II. Present-day mfr. in Easter

DESIGNATION	DENSITY [g/cm³]	T_g[2] [°C]	E_b[3] [°C]	Z_1[4] [°C]	AVERAGE EXPANSIO 20—100 °C	100—200 °C
D 16. Mfr.: VEB SPEZIALGLASWERK EINHEIT, *Weisswasser, formerly* OSRAM-GLASWERK (*cf. D 8*)						
Magnesia glass	2.50	512	555	674	84	95
[10.2] 122p	2.48	517	554	676	86	100
123a M glass	3.09	436	480	611	81	90
352	2.84	458	508	635	88	98
362a	2.36	553	592	775	39	40
584x	2.49	528	570	686	80	97
637a Mo glass	2.40	587	630	791	46	48
D 17. Mfr.: VEB GLASWERK FISCHER, *Ilmenau* (*cf. D 3*)						
Fischer Prima glass	2.51	520	552	686	83	95
Gege-Eff glass	2.57	552	589	702	76	85
D 18. Mfr.: VEB GLASWERK GRENZHAMMER						
HO/240	2.44	518	559	692	81	89
IS/260	2.49	523	568	690	84	99
3/280	2.49	530	569	695	80	96
D 19. Mfr.: VEB GLASWERK HASELBACH						
CT 650b	2.51	514	556	680	87	99
Mg glass	2.49	508	548	670	90	99
D 20. Mfr.: VEB GLASWERK ILMENAU, *formerly* ALT, EBERHARD UND JÄGER (*cf. D 1*)						
A glass	2.56	568	610	737	67	72
AT glass pots	2.48	535	576	718	82	92
AT glass tanks	2.47	527	570	705	83	95
Lead glass	3.10	443	484	604	87	96
N glass (standard glass)	2.57	537	578	695	82	85
D 21. Mfr.: VEB GLASWERK SCHMIEDEFELD						
Chemical technical glass	2.50	535	575	703	89	96

Germany (GDR)[1]

COEFFICIENT [10^{-7}/°C]			$T_{\varkappa 100}$	CLASSIFICATION			NOTES
200—300 °C	300—400 °C	400—500 °C	[°C]	DIN HYDROL.	DIN ACID	DIN ALKALI	
101	109	118	142	V	II	II	
106	111	117	205	IV	II	II	
92	93	—	330	III	III	III	
102	107	—	274	IV	I	II	
39	38	38	321	I	II	II	
102	109	118	232	III—IV	III	II	
47	48	47	231	I	III	III	
101	103	106	225	III	I	II	Tubes: 1 red and 1 white stripe
90	94	97	151	III	I	II	Tubes: 1 red and 1 blue stripe
93	96	99	195	IV	II	II	
103	107	109	159	IV	II	II	
99	103	105	170	IV	I	II	
103	109	120	190	III	II	I	
103	110	119	146	IV	II	II	
74	75	76	177	I	II	II	
96	100	105	219	III	I	I—II	
98	103	106	201	IV	I	I—II	
102	107	—	318	IV	II—III	III	
92	96	102	166	III	II	II	Tubes: 2 yellow stripes
102	107	110	179	III—IV	III	I	

[10.2]

TABLE T 10–4 *(continued)* II. Present-day mfr. in Eastern Germany (GDR)[1] *(continued)*

DESIGNATION	DENSITY [g/cm³]	T_g[2] [°C]	E_b[3] [°C]	Z_1[4] [°C]	AVERAGE EXPANSION 20—100°	AVERAGE EXPANSION 100—200°
D 22. Mfr.: VEB SCHOTT, *Jena* (*cf. also D 9*)[8]						
16III Normal glass	2.58	550	589	693	80	83
[10.2] 59III [5]	2.37	551	—	—	60	—
1447III Mo glass	2.48	533	569	695	50	55
1639III Mo glass	2.31	532	570	705	46	48
1646III W glass	2.34	540	600	743	41	45
1650III Minos glass[5]	3.61	415	—	—	90	—
2954III	2.41	593	628	761	59	63
2962III Pt glass	2.45	518	560	683	80	88
3058III Supremax	2.51	738	775	949	33	37
3061III Na-resistant glass[5]	3.21	545	—	680	81	—
3072III apparatus glass G 20	2.40	558	608	779	46	49
3079III Sealing Pb glass	3.11	480	523	628	81	87
4116III Mo Uviol glass	2.37	608	642	817	54	56
4225III Rasotherm glass	2.24	554	620	800	31	31
4246III apparatus glass G 52	2.42	594	634	793	48	51
5036III Black Uviol glass UG 2[5]	2.58	520	—	690	81	—
Tempax glass	2.30	537	608	776	37	38

Schott intermediate glasses[5]

Type	T_g °C	α (20—100 °C) 10^{-7}/°C	Type	T_g °C	α (20—100 °C) 10^{-7}/°C
C 1	900	8	C 5	663	21
C 2	820	9	C 6	640	26
C 3	760	12	C 7	562	30
C 4	725	15	C 8	542	35

COEFFICIENT [10^{-7}/°C]			$T_{\varkappa 100}$	CLASSIFICATION			NOTES
200—300 °C	300—400 °C	400—500 °C	[°C]	DIN HYDROL.	DIN ACID	DIN ALKALI	
88	93	94	152	III	I	II	Tubes: 1 red-brown stripe
—	—	—	—	I	—	—	
56	57	58	181	I	III	III	
48	49	49	217	IV	III	III	
45	45	45	227	III	II	III	
—	—	—	351	—	—	—	For capacitors[6]
66	66	69	140	I	III	II	Tubes: 1 black stripe
90	93	96	180	III	II	II	
40	43	44	510	I	III	III	For W sealing, rod up to 1 mm dia.; see also Fig. B 10-89
—	—	—	—	—	—	—	For Na-vapor lamps
47	47	47	213	I	I	II	Tubes: 1 black stripe; for Mo up to 1 mm dia.
94	96	—	350	II	III	III	For Pt up to 3 mm dia. and Dumet wire seals
57	55	54	351	I	I	II	Transparent to UV
31	28	28	222	I	I	II	
51	51	52	159	I	I	I	See also Fig. B 10-89
—	—	—	—	—	—	—	Transparent to UV, not to visible light
39	37	38	212	I	I	I	See also Fig. B 10-89

[10.2]

Type	T_g °C	α (20—100 °C) 10^{-7}/°C	Type	T_g °C	α (20—100 °C) 10^{-7}/°C	
C 9	534	38	C 13	562	62	From WHEAT
C 10	558	46	C 14	555	73[7]	
C 11	514	50	C 15	548	73[7]	
C 12	551	60	C 16	505	80	

TABLE T 10–4 *(continued)* II. Present-day mfr. in Eastern Germany (GDR)[1] *(continued)*

DESIGNATION	DENSITY [g/cm³]	T_g[2] [°C]	E_b[3] [°C]	Z_1[4] [°C]	AVERAGE EXPANSION 20—100 °C	AVERAGE EXPANSION 100—200 °C
D 23. Mfr.: VEB SCHOTT, *Gehlberg, formerly* GUNDELACH (*cf. D 6*)						
[10.2] Thüringer glass	2.51	545	582	695	86	96
D 24. Mfr.: VEB GLASWERK SOPHIENHÜTTE, *Ilmenau* (*cf. D 12*)						
177	2.47	520	565	689	85	98
SIN glass 17	2.51	563	600	736	57	64
D 25. Mfr.: VEB GLASWERK STÜTZERBACH; *formerly* GREINER UND FRIEDRICHS (*cf. D 5*)						
Apparatus glass 399	2.50	532	573	690	87	96
R glass	2.45	568	618	773	55	56
For purposes of comparison: CORNING PYREX GLASS (see also Table T 10–4, A 1)						
7740	2.24	543	590	794	34	34

[1] The values in Group II were very kindly supplied by VEB ZENTRALLABORATORIUM DER GLASINDUSTRIE DER DDR, Ilmenau (see also HÜBSCHER): they were determined by uniform methods (see also the following footnotes) with the exception of those types in D 22 numbered: [5]

[2] T_g = transformation temp. obtained from the photographically-displayed expansion curve with a heating rate of 4°/min, as the point of intersection of tangents to the curvilinear portion of the characteristic (see Fig. B 10-7, curve II).

[3] E_b = temperature where softening begins (for definition see Table T 10–5, No. 6), determined from the expansion curve taken with a LEITZ dilatometer, 12 g spring loading (compressive) at 4°/min heating rate.

[4] Z_1 = viscosity temp.: definition see Table T 10–5, No. 8.

[5] Information supplied by VEB SCHOTT UND GEN., Jena.

[6] $\varepsilon = 7.5 - 8$; $\tan\delta = 5 - 6\times10^{-4}$ at 1 Mc/s; $= 25\times10^{-4}$ at 10^9 c/s (see also Fig. B 13-9).

[7] In this range, 20—100°, the expansions of a few adjacent intermediate glasses practically overlap; as a result of their different temp. coefficients, however, large divergences in average expansion coefficient exist if the *whole* expansion range is considered.

COEFFICIENT [10^{-7}/°C]			$T_{\chi 100}$	CLASSIFICATION			NOTES
00—300 °C	300—400 °C	400—500 °C	[°C]	DIN HYDROL.	DIN ACID	DIN ALKALI	
102	105	107	160	IV	II	II	
102	107	112	193	IV	I	II	
62	70	71	207	I	I	II	Tubes: 3 red stripes
101	104	111	203	III—IV	II	II	
56	58	57	253	I	II	II	Tubes: 2 blue stripes
32	32	32	241	I	I	II	

[10.2

(8) Mechanical properties of a few Schott glasses (information supplied by the mfr.).

DESIGNATION	TENSILE STRENGTH σ_{zB} (kg/mm²)	COMPRESS. STRENGTH σ_{dB} (kg/mm²)	BEND STRENGTH σ_{dB} (kg/mm²)	IMPACT BEND STRENGTH a_n [cm/kg / cm²]	YOUNG'S MODULUS E (kg/mm²)	MARTENS-RITZ HARD-NESS (g)
16III standard glass	11.5	83	5	2.1	6600	54
59III	13	94	—	—	7260	—
1447III Mo glass	12.5	75	6	—	7300	61
1639 Mo glass	13	—	—	—	7300	—
2954 thermometer glass	13	92	7.5	2.4	7600	58
2962 Pt glass	12.5	80	7	—	7400	—
3058 Supremax	13	95	8	2.7	9050	59
3072 (apparatus glass 20)	15	91	6	2.8	7500	57
3079 Pb glass	—	—	4.5	—	—	—
3891 Duran	10.5	96	6	2.8	6750	60

E. English glasses

TABLE T 10–4 *(continued)* — *E 1. Mfr.*: BRITISH THOMSON-HOUSTON

DESIGNATION	γ	α 50—400 °C [α 20—350 °C]	T_g[4]	TEMPERATURE FOR VISCOSITY η				
				$10^{14.6}$ (Str. P.)	$10^{(2)}$ (Ann. P.)	10^{12}	$10^{7.6}$ (Soft. P.)	10^{4} (Work P.)
	[g/cm³]	[10^{-7}/°C]	[°C]	[°C]	[°C]	[°C]	[°C]	[°C]
C 9	2.25	36.5[9]		480	525	575[7]	775	
C 11	2.32	45.5[9]	(530)	500[3]	575[3]	605[7]	795	
[10.2] **C 12**	3.06	91[9]	360	380	435	465[7]	630	960
C 14		39[1] [9]	660[71]	680	720–745 [7]	[7]		
C 19	2.48	95[9]	550		530	550[7][8]	710	1025
C 22	2.45	104[9]	530		505	525[7]	680	
C 31		[97][9]			442	[7]		
C 37	2.55	42.5			760	790	(10^{11}P:820°C)	(10^{10}P;850°C)
C 38		≈ 32[9]	≈ 450		505	[7]		
C 40	2.25	48.5[9]	(480)	455	505	535[7]	710	—
C 41	3.01	128			450	475	625	860
C 42		[62]	570		[7]	[7]		
C 43		[72]	505					
C 44		[84]	530		[7]	[7]		
C 46	2.62	43			775	805	(10^{11}P:840°C)	(10^{10}P;875°C)
C 53		≈ 35[9]	≈ 720		[7]	[7]		
C 54	2.95	94.5			470	500	(10^{11}P:530°C)	(10^{10}P;560°C)
C 73	2.95	98.5			470	500	(10^{11}P:530°C)	(10^{10}P;560°C)
C 76	2.98	115[9]			480	505	660	935
C 84		[68]			585			
C 93		76[5]						
D 2		0—400 °C 139		[at 450 °C $\eta = 10^{13.1}$ P; at 500 °C $\eta = 10^{10.6}$ P]				
D 5		122		[at 450 °C $\eta = 10^{12.8}$ P; at 500 °C $\eta = 10^{10.6}$ P]				
D 6		133		[at 450 °C $\eta = 10^{12.5}$ P; at 500 °C $\eta = 10^{10.1}$ P]				
D 7		127		[at 450 °C $\eta = 10^{12.8}$ P; at 500 °C $\eta = 10^{10.6}$ P]				
Press glass		93	500					938
R 48		[13][9]						
R 49		[18][9]						
R 50		[23][9]						
R 45		[9]	≈ 750					

(1) From [1]VOLF.

(2) The annealing point as usually defined ($\eta = 10^{13.4}$ P) lies about 10—15° high.

(1) From PARTRIDGE.

(4) Determined by the knee in the expansion characteristic.

(see DALE, PARTRIDGE)

$\log_{10}\varrho$ [Ω-cm] at 150 °C	$\log_{10}\varrho$ [Ω-cm] at 300 °C	ε 1 Mc/s	$\tan\delta \times 10^4$ 1 Mc/s	YOUNG'S MODULUS [kg/mm²]	PHOTO-ELASTIC CONSTANT [BREWSTER]	NOTES
11.0	7.8[10]	4.2	13	6300	3.7	Borosilicate glass for W
11.7	8.5					Borosilicate glass for Mo
12.3	8.6[10]	6.3	8	6200	2.9	Soft Pb glass for NiFe 50 and Dumet
(14.7)	10.9[10]					$T_{\varkappa 100} = 500°$; hard alumo-borosilicate for W
8.4	5.7[10]	6.8	80	7500	2.7	Soda-lime bulb glass for NiFe 50 and ferritic CrFe
8.1	5.7					Soda-lime, automatic production tube glass, fluorescent lamp bulbs For ferritic CrFe
	12.0	4.2 (10^{10} c/s)	90 (10^{10} c/s)			Mo glass for high-pressure Hg lamps
12.4	9.2[10]					$T_{\varkappa 100} = 385°$
11.5	8.1[10]	4.5	16	6000	3.6	Borosilicate for Nilo K and Kovar
11.7	8.1	8.2				Fe sealing glass, Pb-free
(15.9)	11.9	5.9	19			For Mo; alkali-free alumo-borosilicate
						For W; alkali-free alumo-borosilicate[6]
12.3	8.6					Automatic production tube-glass
12.3	8.6					CrFe sealing glass
						Fe sealing glass, Pb-free
						Fe sealing glass
						Seals to mica
						Pb-free Fe sealing glasses, see [5]STANWORTH
13	9.8					Pb-free glass for press seals[11]; $T_{\varkappa 100} = 364°$
						Intermediate glass
						Intermediate glass
						Intermediate glass
						Intermediate glass

[10.2]

(5) Between 50 and 200°.

(6) High softening point bulb glass.

(7) See also Fig. B 10-18.

(8) See also Fig. B 10-20.

(9) See also Fig. B 10-31.

(10) See also Fig. B 10-50.

(11) From [5]STANWORTH.

TABLE T 10–4 *(continued)* *E 2. Mfr.:*

DESIGNATION (γ = DENSITY, g/cm³)	α 20—350 °C [10^{-7}/°C]	THERMAL RESISTANCE ΔT [°C]	T_g [°C]	TEMPERATURE FOR $10^{14.6}$ P (Str. P.) [°C]	10^{13} P (Ann. P.) [°C]	10^{12} P [°C]
G H 1 (Hysil) (γ = 2.25)	33—36(12)			513(11)	556(11)	
G H A (γ = 2.24)	34	320(2) 300(3)			575(8)	610(8)
[10.2] G S 1 (Intasil) (γ = 2.3)	38			575 to 610(7)		
G S 3 see G S B						
G S 4 (γ = 2.23)	44(12)			590 to 620(7)		
G S A						
G S B (γ = 2.23)	10—100 °C 49(10) (12)	240(2) 200(3)		(380–400)	450	500
G S D (γ = 2.30)	10–100 °C 38.7(9) (12)	280(2) 260(3)			570	605
G S C	45	240(2) 220(3)			590(8)	620(8)
G S D (Intasil)	39	280(2) 260(3)			570(8)	605(8)
GWA (GW7) (γ = 2.49)	10—100 °C 87(4) 20—350 °C 91.5(12)	125(2) 120(3)			510(6) 530	540(6) 550
GWB (GW2) (γ = 2.99)	10—100 °C 86 20—350 °C 100(12)	130(2) 120(3)			390(6) 410	430(6) 440

(1) At 5800 Å.
(2) According to the beaker method.
(3) According to the rod method.
(4) Two-thirds of the product lies between 86.4 and 87.6 $\times 10^{-7}$ 1/°C.
(5) From VOLF.
(6) From firm's catalogue.

E 3. Mfr.: GEN. ELEC. Co., *Wembley (mostly*

DESIGNATION	DENSITY [g/cm³]	α [10^{-7}/°C]	ANNEALING RANGE ($\approx T_{str} - T_{an}$) [°C]	SOFTENING TEMPERATURE (1) [°C]	Soft.-P. ($\eta = 10^{7.6}$ P.) [°C]
Amber Neutral		$\frac{20—350\ °C}{75 \pm 2}$	400—580(3)	580 ± 10	
B 8 see X 8			460—530(3)		
F C N		47.5 ± 1.5(6)		575 ± 10	
G S 1		52		625	
G S 2		58		625	
G S 3		66		620	
G S 4		72		625	
G S 5		78		560	
G S 6		84		515	

CHANCE BROS.

VISCOSITY η $10^{7.6}$ P (Soft. P.) [°C]	10^4 P (Work. P.) [°C]	ε	tan δ 10^{-4}	E [kg/mm²]	PHOTO-ELASTIC CONSTANT (1) (BREWSTER)	NOTES
		5.6	42			97.75% SiO_2; substitute for quartz glass
780(8)				6060	3.8	Hard glass for bulbs
						W sealing glass, borosilicate [10.2]
						For Mo
						Intermediate glass
710				5500	4.1	Borosilicate glass for Nilo K and Kovar; $T_{\varkappa 100} = ca.$ 260°
780				6400	3.75	Borosilicate glass for W
760(8)				6400	3.5	Intermediate glass
780(8)				6400	3.8	
640(6)	1030			6500	2.6	Soda-lime silicate glass for CrFe and Pt; bulbs and tubes
710						
610(6)				6000	2.9	Pb glass for Dumet, CrFe and Pt

(7) From PARTRIDGE.
(8) From KOHL.
(9) Tolerance (38—39.4)$\times 10^{-7}$ 1/°C.
(10) 20—300°: 54.5$\times 10^{-7}$/°C.
(11) From REIMANN.
(12) See also Fig. B 10-32.

(data from MANNERS AND OSRAM-GEC*)*

$\log_{10} \varrho$ [Ω-cm] at 00 °C	150 °C	200 °C	300 °C	500 °C	NOTES
					Chemically resistant ampoule glass
					Hand-blown glass
	12.65	10.95	8.9›	—	For Fernico and Kovar
					Intermediate glasses

TABLE T 10–4 *(continued)* *E 3. Mfr.:* GEN. ELEC. CO., *Wembley (mostly*

DESIGNATION	DENSITY [g/cm³]	α [10⁻⁷/°C]	ANNEALING RANGE ($\approx T_{str} - T_{an}$) [°C]	SOFTENING TEMPERATURE (1) [°C]	Soft.-P. ($\eta \approx 10^{7.6}$ P.) [°C]
H 26 X(7)	2.30	20—580 °C 46 ± 1(6)	600—725(3)	780 ± 10	930 ± 15
[10.2] H 428		20—300 °C 32	(—800)	840	
H H	2.33	20—450 °C 47 ± 1(6)	500—590(3)	625 ± 10	780 ± 15
H R 9		20—350 °C 51.5 ± 1.5			
L 1	3.08	20—320 °C 90.5 ± 1.5(6)	340—430(3) 425(4) 445(5)	470 ± 10	610 ± 15
L 14		98	360—430(3)		
M 6		20—350 °C 73 ± 2(6)	450—580		600 ± 10
Na 10		Matches "X 8"		Very low	
R L 16		20—300 °C 114			
S S 3		20—400 °C 94	480—530	555	
W 1	2.25	20—350 °C 37.5 ± 1(6)	540(4) 580(5) 510—570(3)	600 ± 10	760 ± 15
W Q 31		20—300 °C 10	(—750)	750	
W Q 34		20—300 °C 21	(—700)	700	
X 4		20—300 °C 96	465(4) 500(5) 490—520(3)		
X 7		20—300 °C 101	430—510(3)		
X 8	2.50	20—350 °C 96.5 ± 1	465(4) 500(5) 400—520(3)	550 ± 10	690 ± 15

(1) Inversion point in the dilatometer measurement (spring compression).

(2) 52 Fe; 42 Ni; 6 Cr.

(3) The second number is the temperature for $\eta = 10^{13}$ P.

ata from MANNERS AND OSRAM-GEC) *(continued)*

$\log_{10}\varrho$ [Ω-cm] at					NOTES
00 °C	150 °C	200 °C	300 °C	500 °C	
		13.0	11.4	8.8	Alkali-free borosilicate glass for Mo seals in high pressure Hg lamps
					Intermediate glass [10.2]
—	11.7	10.3	8.3	5.9	Borosilicate for Mo sealing
					Press glass with high thermal shock resistance
(13.7)	12.0	10.8	8.6	5.1	Soft Pb glass (30% PbO) for Dumet, CrFe, FeNi 50 and Fernichrome[2] (ϱ from REIMANN)
					For ferritic CrFe
					White neutral glass, machine-drawn tubes
Low					Na-resistant glass, mostly as 25—75 μ sheathing on X 8 glass
					Fe sealing glass
—	11.8	10.5	8.3	—	High insulating resistant, Na-resistant intermediate glass for seals in Na vapor lamps
(13.5)	(12.23)	9.9 (11.04)	8.0	5.6	W sealing glass. Intermediate glass for ceramic (Mullite) to Pyrex
					Intermediate glass for W to quartz glass
					Intermediate glass for W to quartz glass
8.7	7.8	6.9	5.4	3.4	Soft soda glass; ϱ from REIMANN
					Soft soda glass
10.0	(8.8)	6.7 (7.8)	5.3	3.3	Soda glass for ferritic CrFe; devitrification range 815—840 °C

(4) Strain point given by REIMANN.

(5) Annealing point given by REIMANN.

(6) See also Fig. B 10-33.

(7) Dielectric constants for 3.5×10^{10} c/s (from HILLIER): $\varepsilon = 4.1$; $\tan\delta = 120\times10^{-4}$.

TABLE T 10–4 *(continued)* *E 4. English glasses for vacuum purposes; (from* [1]DOUGLAS*)*

DESIGNATION[2]	α 20—300 °C [10^{-7}/°C]	T_g[1] [°C]	TEMPERATURE FOR η = [3] $10^{14.7}$ (T_{str}) [°C]	$10^{13.4}$ (T_{an}) [°C]	$10^{7.6}$ (T_{soft}) [°C]	10^4 P (T_{work}) [°C[	$T_{\varkappa 100}$ [°C]	ϱ_{300} °C [Ω-cm]
(A) Soft soda (for lamp bulbs and inert-gas-filled luminous tubes)	93[5]	—	(480)	510	710	1005[3]	135[4]	$10^{5.3}$
(D) Hard borosilicate (high-wattage lamps, chemical ware)	29[5]	550	—	—	820	1250[3]		
(F) *idem*	36[5]	530	(520)	540	800	1170[3]	300[4]	10^8
(H) Lead glass (sealing, has Pb content)	90[5]	420	410	430	640	980[3]	335[4]	$10^{8.7}$
(J) Extra hard (Hg-vapor lamp envelopes)	43[5]	720	670	710	945	1220[3]	570[4]	$10^{11.4}$
(L) Special glass (resists Na vapor)	—	—	—	—	675	890[3]	—	—

[10.2]

[1] Found from the inflexion point of the expansion characteristic.

[2] Composition in Table T 10–2, E 4. [3] See Fig. B 10-16 for viscosity curves.

[4] See also Fig. B 10-51. [5] See also Fig. B 10-34.

E 6. PLOWDEN AND THOMPSON LTD, *Stourbridge*

DESIGNATION	TYPE	α (0—300 °C) [10^{-7}/°C]	Ann. P. [°C]	NOTES
Dial 36	Borosilicate + high Al_2O_3 content	36	580	Rod for coiling (sheathing) in W sealing technique
Bluesil	Al-borosilicate	37	570	W sealing glass
Dial 43	Borosilicate	42	560	Intermediate glass between W glass and Kovar glass
Kodial	Borosilicate	49	530—540	Kovar and Mo sealing glass[1]
Normal	Soda-zinc	84	560	FeNi sealing glass
Dial 444	Soda glass	88	510	Pt sealing glass
L 1	Lead glass	91	430	See Table T 10–4, E 3
Neon Soda	Soda glass	96	520	CrFe sealing glass
Animals' Eye	Lead glass	113	470	Fe sealing glass

[1] Young's modulus $E = 6360$ kg/mm^2; $T_{\varkappa 100} = 340°$ approx.; $\log_{10} \varrho\ (150°) = 11.85$ approx. $\log_{10} \varrho\ (300°) = 8.39$ approx. (ϱ in Ω-cm); $\varepsilon = 4.96$ (1 Mc/s); $\varepsilon = 4.97$ (100 Mc/s).

TABLE T 10–4 *(continued)* *F. French commercial glasses*

F 1. Mfr.: CRISTALLERIE DE BACCARAT[3]

DESIGNATION	α [10^{-7}/°C]	T_g [°C]	ANNEALING POINT[1] [°C]	$T_{\varkappa 100}$[2] [°C]	DIN HYDROL. CLASSIFICATION	tan δ (20 °C) at 1 Mc/s ($\times 10^{-4}$)[4]	NOTES
E Neutrohm	49	≈ 505	650	322	I	32	For Mo-Kovar
KM		≈ 540	675	323		30	
Moly A 119				223[2]		[4]	
P Neutrohm	≈ 50	≈ 560		340—370	I		For Mo
T Neutrohm	25–350 °C 38	≈ 540	680	332	I	30[4]	For W

[10.2]

[1] Not stated whether upper or lower annealing point.

[2] $T_{\varkappa 100}$ point of other French glasses are in Fig. B 10-53, where the temperature-dependence of electrical resistivity of a series of glasses made by this firm are given.

[3] See also [2]DANZIN.

[4] See also Fig. B 10-73 for tan δ; see Fig. B 10-66 for ε.

TABLE T 10–4 *(continued)* *H. Dutch commercial glasses. H 7. Mfr.*

DESIGNATION	γ [g/cm³]	α 20—300 °C [10^{-7}/°C]	T_g [°C]	TEMPERATURE FOR 10^{14} P [°C]	TEMPERATURE FOR 10^{13} P [°C](2)
111	2.85	(92)(3) (94)(3) **89.5**	*ca.* 425	387	423
[0.2] 122 (29% PbO)	3.05	(87)(3) **90.7**	*ca.* 425	381	421
KIA	3.0	95	*ca.* 425	$10^{14.6}$ P 380	$10^{13.4}$ P 410

DESIGNATION		α [10^{-7}/°C]	T_{str} ($\eta = 10^{14.6}$ P) [°C]	T_{an} ($10^{13.6}$ P) [°C]	T_{soft} ($10^{7.6}$ P) [°C]
Fe sealing glass(4)	+ Pb	116	400	425	605
	no Pb	118	450	470	645

(1) The so-called "softening point" was determined in dilatometer measurements as the irreversible inflexion point in the expansion curve.

Oe. Austrian glasses. Oe 1. Mfr.

DESIGNATION	γ [g/cm³]	α 20—200 °C [10^{-7}/°C]	T_g [°C]	$T_{softening}$(1) [°C]
757 Pb glass				
915a Pb glass N (32% Pb)		100	425	470
1065 lime-magnesia glass		98	485	528
Alkali-free electroglass				
Apparatus glass (AF 1 ?)		≈ 92	—	595
Fe sealing glass "G", high lead		129	385	425
Fe sealing glass "L 1", lead-free, but see Table T 10–2, Oe		115	450	490
Fe sealing glass Z 601a, lead-free		119 (0–400°C:136)	455	490
Mo sealing glass M Mo4		49	550	605
Mo sealing glass M Mo15		51 (20—300 °C)	490	570
Mo sealing glass M VII BT		≈ 45	580	610
V Gl 3, alkali-free Pb glass		62	560	590
W 2 glass, high lead		82	415	460
W glass M W 14		38	480	580 (—610)

(1) Generally determined as the irreversible inflexion point in the expansion curve, caused by compres

PHILIPS GLOEILAMPENFABRIEKEN (see also pp. 652-653)

VISCOSITY η			$T_{\varkappa 100}$	NOTES
10^{12} [°C]	10^{10} [°C]	$10^{7.6}$ [°C]	[°C]	
552	—	624	335	
550	507	—	370	For pumping stems
450—475)(1)	—	630	370 310(5)	For ordinary sealing, similar to the German M glass Osram, or Czech M glass Polubný

[10.2]

T for $1.33\times10^6\ \Omega$-cm	ϱ [Ω-cm]		NOTES
[°C]	50°C	100°C	
370	3×10^{15}	1.5×10^{15}	For dome and pinch-foot in TV tubes(4)
355	7×10^{13}	7×10^{12}	For luminescent screen window of TV tubes(4) to seal to chromed Fe cone

(2) The annealing point T_{an} (for $\eta = 10^{13.6}$ P) is about 15° lower than T for $\eta = 10^{13}$ P.
(3) Individual measurements 1945—1951. (4) From [1]GIER. (5) From [2]KRATOCHVÍL.

MOOSBRUNNER GLASFABRIKEN A.G., *Vienna VI*

SURFACE TENSION [dyne/cm]	$T_{\varkappa 100}$ [°C]	ε	$\tan\delta$ 10^{-4}	HYDROL. CLASSIFICATION	NOTES
241	296			II	Tube glass with high insulation resistance
305	172			IV	For standard hot-filament lamp bulbs
	308				High insulation resistance
255	240			IV	Good insulator
	260				
	250			I	
	300				Borosilicate containing Pb
270	577			I	Very high insulating resistance
222	413	8—9	5—6!	I	High insulating resistance and low dielectric loss
	350			I	Borosilicate containing Pb, with high insulating resistance

sive spring pressure in the dilatometer.

TABLE T 10-4 *(continued)* *S. Russian Glasses*

DESIGNATION	α 25—100 °C [10^{-7}/°C]	TWB [°C] (2)	SOFTENING POINT [°C]	ANNEALING POINT [°C](1)
Ba-Li glass	88		520	(358—456)
BB apparatus glass (B-free)	84—87	130	490—520	470
BD-1 Ba glass	90 ± 2(3)	110	550 ± 10	490 (400—505)
Durobax	48—50	180	700—720	650
Mazda glass	46—48	—	—	—
Pyrex I or II	33—36	230	550—620	580
[10.2] Pyrex P 15	33.4 ± 0.5	—	600 ± 10	(upper 560)
Sverchpireks	29—30	250	850—900	750
S-88-11	89 ± 2	135	570 ± 10	(410—520)
S-88-13	89	130	590 (570)	(405—515)
White glass	80—82	120	510—530	480
ZS 4	88 ± 2(3)	100	490 ± 10	(360—450)
ZS 5 K	49 ± 1	180	575 ± 10	(410—535)
ZS 5 Na	49 ± 1	180	580 ± 10	520 (410—540)
ZS 8 (Mo glass)	48 ± 1	200	555 ± 10	(360—500)
ZS 9	35.5 ± 1.5(3)	220	575 ± 10	(upper 490)
ZS 11	40	240	620	(410—530)
N. 2 (soft bulb glass)	84—87 89 ± 2(3)	105	550 ± 10	470 (410—520)
VI-V glass (lead)	87—90	130	480—500	450
No. 12 lead glass	87—90	130	480—500	450
No. 16	81.5 ± 3	—	525 ± 15	(upper 460)
No. 17	39.5 ± 1(3)	230	640 ± 10	(410—540)
No. 23 laboratory glass	89 ± 2(3)	115	580 ± 10	(410—530)
No. 35 Mo glass	54 ± 1.5	170	590 ± 10	520 (440—555)
No. 36	82 ± 2(3)	130	610 ± 10	(425—545)
No. 40	37.5 ± 1.5(3)	185	806 ± 10	(580—750)
No. 46 Mo glass	47 ± 1(3)	200	590 ± 10	550 (420—555)
No. 55 UV	89 ± 2		530	—
No. 59 thermometer glass	60—62	150	530—610	550
No. 94	90 ± 2		535	—
No. 112 barium glass		130	510—540	490
No. 401	82.5 ± 0.5	130	600	(upper 560 ± 10)
No. 402	87 ± 2	125	585	(410—535)
No. 846 standard laboratory glass	60—62	150	530—610	550

(1) Single values useful only for comparative purposes; bracketed values = limits of the annealing range or upper anneal temp. from KOROLEV or LJUBIMOV.
(2) TWB = thermal shock resistance. (3) From BORŠČEVSKIJ.

TABLE T 10-4A *Properties of a few phosphate glasses*

DESIGNATION	α 20—300 °C [10^{-7}/°C]	α 20—500 °C [10^{-7}/°C]	T_g [°C]	TEMP. °C FOR $\eta = 10^{13}$ P	10^{12}P	10^{11}P	10^{10}P	$T_{\chi 100}$ [°C]	ϱ_{300} °C [Ω-cm]	NOTES
Highly insulating glass no. 14(1)	57	62	610 (2)	623	642	657	690 (3)	650	$10^{12.6}$ (4)	3STANWORTH
X-ray shielding glass	see Table T 10-11									

(1) Composition see Table T 10-2A. (2) Determined by inflexion point in expansion characteristic.
(3) See also Fig. B 10-20. (4) See also Fig. B 10-52.

TABLE T 10-4B *Properties of a borate glass*

DESIGNATION	DENSITY [g/cm³]	X-RAY ABSORPTION COEFF. μ [1/cm]	MASS ABSORPTION COEFF. μ/ϱ [g/cm²]	NOTES
Lindemann glass	2.026	For 0.1 Å: 0.296	For 0.1 Å: 0.146	From MOREY; see also Figs. B 5.6-3 and B 5.6-4

10.2. Physical and Chemical Properties

Table T 10–3 gives a general survey of the characteristic properties of the most important groups of glasses. Table T 10–4 gives a detailed collection of the properties of technical glasses arranged by manufacturer.[7] The chief properties are treated more exactly in the sections which follow.

10.2.I. *Mechanical Properties*

([1,3]GEHLHOFF, PRESTON, [1]STANWORTH)

Glasses under load do not behave like metals, which first follow elastically the tensile or compressive forces, then flow, and finally rupture; the flow process is completely absent for glass. Correspondingly, glass supports satisfactorily any load that is applied slowly and is not too great, because of its relatively high elastic modulus,[8] but it readily breaks under shock loading, especially when crystaline inclusions[9] are present due to devitrification, or when there are thermal strains. [10.2]

Fig. B 10-3 Vacuum switch with glass spring; lateral pressure on the outer switch arm (right) permits small movements of the switch in the vacuum [from BOSCH] (made by SIEMENS)

A relative index of the strength of various glasses against shock loading, and hence of "brittleness" is obtained by allowing an ivory ball suspended like a pendulum to strike glass bulbs; the angle of swing needed to break the bulb is measured. Since *impact strength* depends strongly on the glass thickness (cf. [2]GEHLHOFF), this must be measured carefully at the point of impact after breakage.

As regards the determination of strength values in particular cases and the conclusions that follow, the following points should be observed: because of the wide variation between individual values (due to surface defects and the resulting stress concentrations) only statistical averages are used in all strength property data. Since, in addition, annealing strains have a powerful influence on the corresponding measurements, only values obtained on well-annealed test-pieces can be used. However, the composition of the glasses generally has no effect worth mentioning on the purely mechanical properties.

The *tensile strength* of technical glasses is relatively low compared with metals (cf. Fig. B 10-4); they lie between 3 and 15 kg/mm^2 (see also Tables T 10–3 and T 10–4, note [8]) but increase considerably for very thin test-pieces (glass fibers) as the diameter drops (see Fig. B 10-5). Determination of tensile strength is carried out as a rule on 5 cm length, solid glass rods of 3–4 mm dia., which should be set in the tensile tester

[7] The serial order of Manufacturers and glasses in Table T 10–4 is the same as that in Table T 10–2 (glass compositions given where known) in order to facilitate cross-referencing to the corresponding composition.

[8] This property is used in making long tubular vacuum lines (KUNDT glass springs) or in short corrugated tubes (elastic bodies, see, e.g., Fig. B 10-3).

[9] In the case of opal glass bulbs, which are purposely clouded by precipitated fluorides, the impact strength and thermal shock resistance depend strongly on the size and type of the particles of fluoride, which in turn depend on the thermal treatment ([2]GEHLHOFF).

without any non-axial loading. (Further details, see, e.g., [3]GEHLHOFF, [2]SPRINGER.) In vacuum technology, adequate reliability can be achieved in calculations by allowing

[10.2]

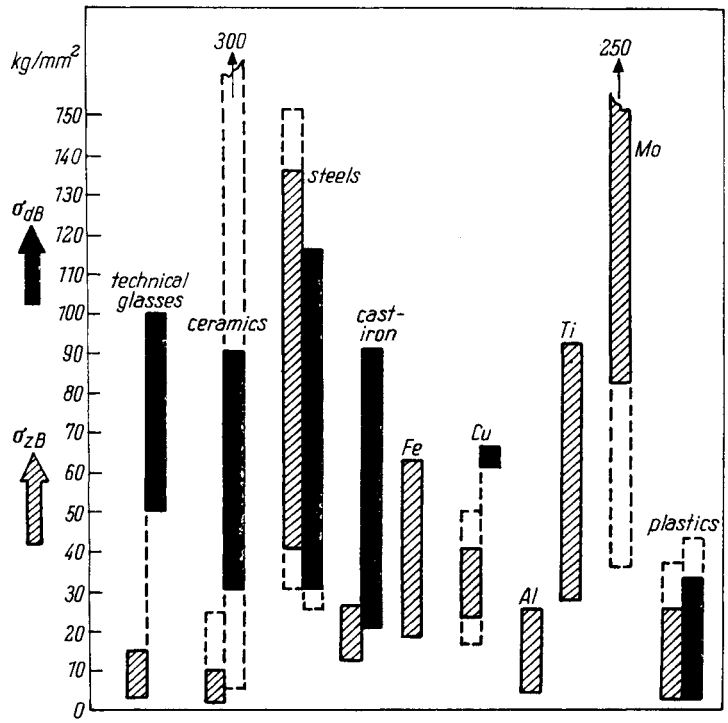


Fig. B 10-4 Comparison of the tensile strength σ_{zB} and compressive strength σ_{dB} of technical glasses with values for other materials ([4]ANON.)

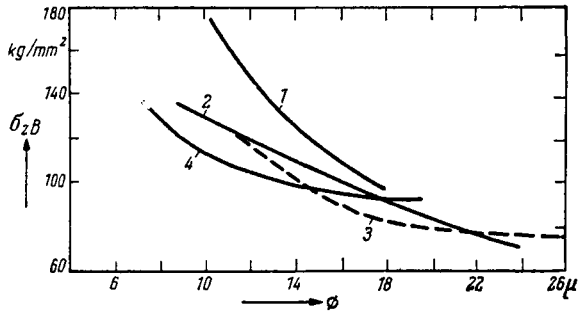


Fig. B 10-5 Tensile strength σ_{zB} of glass fibers as a function of diameter of fiber; curves 1–4 are for various types of glass measured by various authors

a maximum continuous loading in tension of 0.6–0.8 kg/mm², and with carefully annealed glass 1–2 kg/mm², according to the shape of the piece.

The *compressive strength* of annealed glass is almost 10 times larger than the tensile, a fact of great importance in glass-metal sealing (see Chapter 30). Values for technical

glasses lie between 50 and 125 kg/mm² (see Tables T 10–3 and T 10–4, note[8]) and can thus compete with those of metals (see Fig. B 10-4). Measurement is mostly carried out on square glass plates 4 × 4 mm² and 1.5–2 mm thick in a hydraulic press with ball loading. The results are only reliable if the glass plate under test fractures explosively to dust with a loud crack.

See [1]ASTM, [2]SPRINGER on the measurement of *bending strength* of glasses. A few figures can be found in Table T 10–4, note[8], both for this and for the *impact bend strength.*

Young's *modulus of elasticity* is usually found by flexure of rods of T 4–10 mm dia.; they are laid on two blunt knife-edges spaced *ca.* 200 mm apart, and loaded centrally. [10.2] For further details see [1]ANON., [2]SPRINGER. This modulus is of importance not only in purely mechanical processes, but also thermal ones, since it determines the magnitude of the tensile or compressive stresses which occur when the volumetric changes associated with temperature variation cannot take place without constraints; this can happen, for example, in sealing. Quantitative data for technical glasses are given in Table T 10–4, A 1, and note[8] (SCHOTT glasses).

POISSON's ratio μ is important in calculation of stresses in glass-metal seals, and gives the ratio of transverse contraction to axial expansion under load. Its value generally lies between 0.20 and 0.25 for technical glasses, but can usually be taken with sufficient accuracy as 0.22.[10] The value seems to fall as the transformation temperature rises ([1]GEHLHOFF).

The mechanical *hardness*[11] as a measure of workability obviously cannot be determined as in metals by plastic strain as in Brinell tests. Instead, the method is often to measure the resistance shown by the glass to penetration of a conical diamond moved over the surface under fixed test conditions. In the so-defined "Martens scratch hardness", the numbers given (see, e.g., Table T 10–4, note[8], SCHOTT glasses) refer to the load in grams needed to produce a scratch width of 0.01 mm. Other makers measure the "impact abrasion resistance" to the effects of a standardized grit blast; the value for plates of soda-lime glass is set at unity. Some values for this are given in Table T 10–4, A 1 (CORNING). As can be seen, Pb-glasses are generally softer than soda-lime glasses, while borosilicates exhibit the largest abrasion resistance.

WILLOT defines the "grinding hardness" as the reciprocal of the volume of glass removed per minute by grinding with a particular unbonded grinding agent under standardized conditions. The value is related to quartz glass (= 1000).

In the case of large tubes and envelopes, and especially in recent years TV tubes, there is an ever-increasing need to determine the "implosion strength". To test this, the prepared tubes are placed in sealed containers and subjected to gradually increasing external pressure (air or water of fixed temperature from 1 to 10 atm gauge) and possibly to bursting point (see Fig. B 10-5A). The device is often lightly rubbed with emery cloth before testing in order to imitate the surface damage which normally appears in use and which, as is well known, strongly influences the strength properties. In the case of *water pressure* testing, the evacuated tube for test is immersed in a water tank. The tank is then sealed and the water surface subjected to slowly increasing air pressure. Even unworked envelopes or bulbs can be given an acceptance test at the

[10] For metals, μ is mostly > 0.25, more often about 0.33.

[11] Separation of glasses into hard and soft groups has therefore nothing to do with *mechanical* hardness.

TABLE T 10-5. CHARACTERISTIC POINTS (USED IN PRACTICE) ON THE VISCOSITY CURVES OF A GLASS (CF. FIG. B 10-6)

NO	DESIGNATION	VISCOSITY (P)	DEFINITION	SYMBOL (8)
1	Transformation range	10^{14}–10^{13}	Limiting range between brittle and viscous state	
[10.2]	Transformation point T_g	$10^{13.3}$ ($= 2 \times 10^{13}$)	(a) inflection point of expansion curve $\Delta l/l = f(T)$ (1) (2) (b) inflection point of resistance-temp. function $\log \varrho = f(1/T)$ (T in °K) (1) (3)	$V_{13.3}$
2	Strain point T_{str}, 15 hr stress-relieving temp.	$10^{14.5}$ ($=3.2 \times 10^{14}$) (5)	Temp. at which glass under stress will be annealed reliably in 15 hr	$V_{14.5}$
3	Setting point T_{set}, or tempering point (only for glass-metal seals)	*ca.* 10^{14}	Temp. used as general starting point for comparison of the contraction curves of both partners of a glass-metal seal to draw inferences about size and direction of stresscs during and after cooling and later heating in operation (see Chapter 30)	V_{14}
4	Annealing point T_{an}, 15 min stress-relieving temp.	$10^{13.0}$ (6)	Temp. at which a glass under internal stress will anneal reliably in 15 min ([3]LITTLETON)	V_{13}
5	Rapid annealing temp. T_0, instantaneous annealing point	Just under 10^{13}	Temp. at which internal strains are equalized almost at once (in about 2 min). T lies *ca.* 15° above annealing point	$V_{12.8}$
6	Temp. E_b at which softening begins	*ca.* 10^{12}	Temp. at which reversal of the expansion curve is just visible in the straight part of the leg above the transformation range (see Fig. B 10-7). This is caused by support spring of the dilatometer	V_{12}
7	Deformation point M_g	$10^{11.5}$–10^{11}	Highest temp. at which record of expansion can be obtained in the dilatometer (see Fig. B 10-7) before the test-piece is compressed by the spring. Stress equalization takes place in *ca.* 15 sec at this temp.	$V_{11.5}$
8	Viscosity temp. Z_1 according to SCHOTT; see, e.g., Table T 10-4, D 16–D 25	*ca.* 10^{8}	Temp. at which a glass fiber 0.3 mm dia. under 1 g/mm² load lengthens by 1 mm/min (hot zone of furnace 40–50 mm, heating rate 10°/min	V_8
9	Softening point T_{soft} (CORNING), Littleton point	$10^{7.65}$ ($=4.5 \times 10^{7}$) (7)	Temp. at which glass perceptibly begins to deform under its own weight; usually measured by finding the temp. at which a rod ($\gamma \approx 2.5$ g/cm³) 0.6 mm dia. and 229 mm long elongates under its own weight by 1 mm/min when the upper 100 mm is heated in a furnace at 5–8°/min ([2]LITTLETON)	$V_{7.65}$

TABLE T 10–5 *(continued)*

NO.	DESIGNATION	VISCOSITY (P)	DEFINITION	SYMBOL (8)
10	Sintering temp. (VOLF)	10^6	Temp. at which lightly compressed glass powder will sinter to a compact piece	V_6
11	Flow point	10^5	See [5]LILLIE	V_5
12	Working point T_{work}	10^4	Temp. at which glass is soft enough to be worked by most of the normal methods (blowing, pressing)	V_4
	Upper limit of "working range"[4]	10^3	The working range corresponds to a temp. range where the viscosity is *ca.* $10^{7,6}$ to 10^3 P	V_3
13	Liquidus temp.	$10^{2.5}$	Devitrification not possible above this temp.	$V_{2.5}$
14	Melting point T_{melt}	10^2	Temp. at which glass is considered a fluid	V_2
	Melting range	$10^{2.5}$–$10^{1.0}$	Limits for practical use for furnace melting	

[10.2]

(1) Generally undertaken at a heating rate of 2–4°/min.
(2) Fig. B 10-7.
(3) Fig. B 10-45.
(4) From MÜLLENSIEFEN.
(5) Recent viscosity values by [2]LILLIE (so far taken at T_{str}: $\eta = 10^{14.6} = 4 \times 10^{14}$ P).
(6) Recent viscosity values by [2]LILLIE (so far taken at T_{an}: $\eta = 10^{13.4} = 2.5 \times 10^{13}$ P).
(7) [3]LILLIE.
(8) Proposed at the Glass Conference 1955 in Hradec Králové.

desired pressure if their openings are closed with a rubber stopper and the test pressure is about 1 atm lower than for evacuated tubes. See OSTRANDER for further details of such methods.

See COHEN on the measurement of compressive and tensile stress zones in glass of TV tubes by means of resistance strain gauge tape, in the pressure tank.

10.2.II. *Viscosity*

If glass is heated, it does not show a definite M.P. as in metals, but once above the so-called transformation temperature, a fixed point, it rapidly becomes softer, and the viscosity falls with rising temperature rather as shown in Fig. B 10-6 (schematic). Compare also the experimental viscosity curves of Figs. B 10-5 to B 10-20. Knowledge of the viscosity characteristic of a given type of glass or at least of some "characteristic points" on it, is of great importance, not only in manufacture (melting and degassing in the furnace, casting, drawing-off, pressing) but also in working by torch (flame temperature, burner setting, annealing *after* forming) and for use in vacuum technique (max. operating temperature, softening during the pumping schedule).

Table T 10–5 is a collection of these characteristic viscosity points as used in vacuum and glass technology, which are often given by the manufacturer, and which have

mostly been given a special name. In particular, the following should be stated here: up to a certain temperature, which for "soft" glasses generally lies between 400 and 500°, for "hard" glasses above 500°, the transformation temperature T_g mentioned above, the glass is in the so-called brittle state where only very small relative movement of the glass particles (molecules) is possible, so that equalization of any stresses present in the piece is virtually impossible. Above the T_g point the glass goes over reversibly into the "viscous" or ductile state as the temperature rises, and for a 25° step, the viscosity falls by about an order of magnitude (see Fig. B 10-20), the glass particles become increasingly mobile, and stress relief can therefore take place the more rapidly the higher the temperature chosen. Too high a temperature should not be chosen or deformation occurs due to the weight of the specimen, especially if it is thin. Knowledge of T_g for a glass is therefore of great importance for all stress-relief processes, e.g. after flame-working and after making glass-metal seals. Unfortunately, it is not a simple matter to fix the transformation point. It is certainly not correct to describe it simply, as used to be done, as the "temperature boundary of the brittle and viscous states" (with a viscosity of *ca.* 2×10^{13} P $= 10^{13.3}$ P), since with prolonged heat treatment periods, stress relief can be achieved even at temperatures below the temperature thus defined; nor is it an appropriate definition, since the viscosity in the transformation region is a strong function of previous heat-treatment of the test-piece (see, e.g., [2]DALE, FANDERLIK). Most of the figures for transition temperature of glasses in manufacturers' catalogs are based on the observation that the expansion curve of any annealed glass in the transformation region shows a fairly marked kink, which proves to be reversible when the sample is heated up and cooled (see Fig. B 10-7). The transition temperature is then defined as the intersection of tangents to the expansion curve above and below the kinked zone (curve I) or, more recently, as the contact point of the circle of osculation with the bend in the characteristic. In the latter case, this is given by the intersection point T_g of the bisector ε of the angle between the tangents v_1 and v_2 to the expansion characteristic above and below the transformation range with the function itself.[12] Also, the fact that the electrical resistivity function changes slope in the transformation range is used to determine the transition temperature; the fairly sharp knee in the plot of $\log \varrho = f(1/T)$ is found (ϱ = elec. res. in Ω-cm, T = temp. in °K, cf. also Fig. B 10-45, [1]BERGER).[13] The results of measurements by both methods

[10.2]

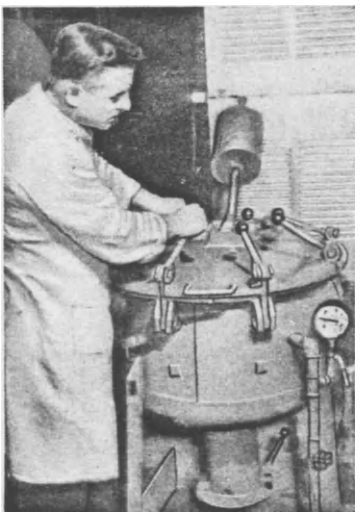


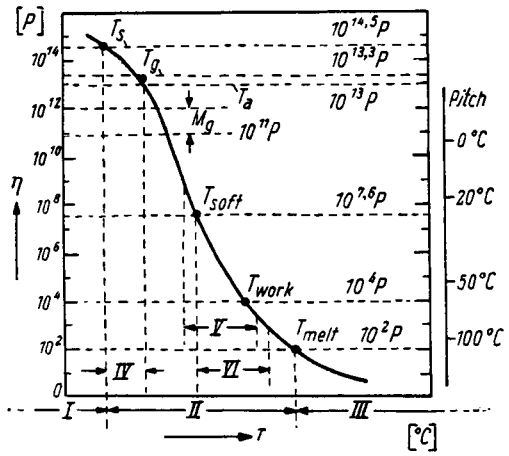
Fig. B 10-5 A Water pressure testing on evacuated TV tubes with 2 atm pressure in a test tank (from C. LORENZ A. G.). Testing time: a few minutes.

[12] T_g' naturally lies a few C° lower than the previously defined T_g.

[13] See WARTENBERG on the determination of the transition temperature by measuring the maximum (up to bursting point) internal pressure that glass tubes can sustain.

agree to $\pm 5°$ ([1]BERGER), but depend somewhat on the rate of heating during the taking of data.[14]

As a result of this, it has become more and more the accepted procedure to give, rather than the transition temperature, the corresponding but better defined points on



[10.2]

Fig. B 10-6 Schematic viscosity diagram for glass

T_g = transformation temperature; T_{str} = 15 hr stress-relief temperature; T_{an} = 15 min stress-relief temperature; M_g = deformation temperature (range); T_{soft} = softening temperature; T_{work} = glass-working temperature; T_{melt} = melting temperature. *I* brittle range; *II* viscous range; *III* liquidus range; *IV* stress-relief range; *V* working range; *idem* in blow-lamp: $\eta = 10^{8,6}$ to 10^6 P; *VI* devitrification range. At the right-hand ordinate, the temperatures for the corresponding viscosities of pitch (asphalt) are given for comparison

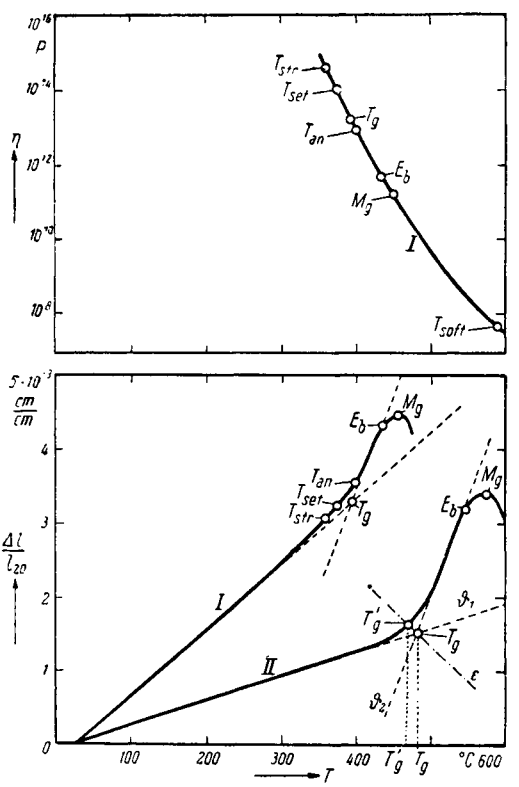


Fig. B 10-7 Expansion curves $\Delta l/l_{20} = f(T)$ of two annealed technical glasses, taken in a quartz dilatometer with a heating rate of 2°/min. Upper fig.: corresponding viscosity curve as a temperature function, for glass I

T_{str} = strain point; T_{set} = setting point; T_{an} = annealing point; T_g or T_g' = transformation point as determined from dilatometer; E_b = temperature at which softening begins; M_g = deformation point, as found from dilatometer readings; T_{soft} = softening point

[14] The dynamically measured transition temperature (heating rate 4°/min) is about 15–30° higher than the statically measured point (SCHOTT): however, almost the same value is found at any rate of heating, from 1 to 5°/min.

the viscosity curve, which are of more direct value in practice. It is freely admitted here that, in contrast to the transition temperature, which has a definite *physical* significance, the definitions of these points are more or less arbitrary and are made to suit the specific purposes of the case in question. Consequently, the individual manufacturers often prefer quite different viscosity numbers. Some firms, on the other hand, generally avoid giving "characteristic viscosity points", and provide besides the transition temperature the values of viscosity (in the range 10^{12} to 10^{9}) for each power of ten individually (e.g. OSRAM-Berlin, Table T 10–4, D 8).

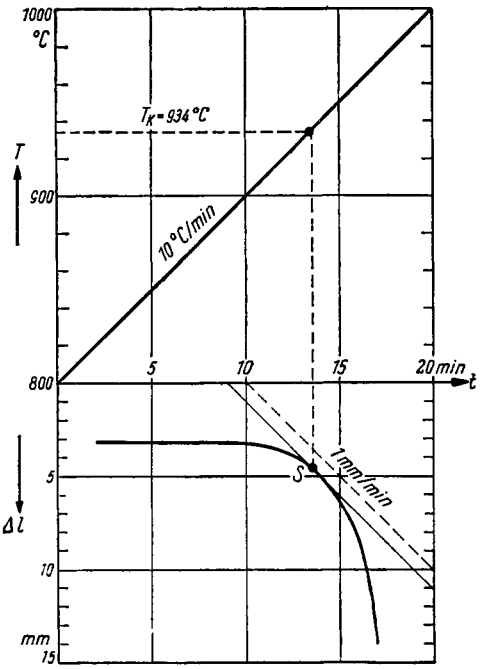
[10.2] The characteristic viscosity points preferred in practice are primarily the "strain point" T_{str} (in German: 15-Stunden-Entspannungstemp.) with a viscosity of $10^{14.5}$ P[15] and the "annealing point" T_{an} (in German: 15-Stunden-Entspannungstemp.) with a viscosity of $10^{13.0}$ P[15]; that is to say, those temperatures at which artificially strained glasses lose their strains down to 10% of the original value, i.e. are to all intents and purposes, annealed in 15 hr or 15 min respectively. These points are not only precisely defined, but moreover correspond to the requirement of practice in a most effective way (establishing temp.–time annealing schedules after forming, see 10.3.VIII). Of course, their precise determination[16] requires considerable expense in equipment (see below). Many firms make do by specifying an easily measured "softening point".[17] This should generally be understood to mean the temperature M_g of the peak (reversal point of the expansion curve, deformation temp., see Fig. B 10-7) or the temperature E_b where compression just begins when measuring the thermal expansion characteristic in a quartz dilatometer as in Fig. B 10-24. In this case the glass rod under test is axially compressed (shortened) irreversibly above a certain temperature, as a result of pressure applied by a metal support spring or weight. Obviously, the values M_g or E_b depend on the dimensions of the test-piece (usually not given in the literature or catalogs) and on the spring rate of the support of the dilatometer in question. Such results at best only allow comparisons to be made between glasses of the same manufacturer. The "viscosity temperature" Z_1 given for glasses in Table T 10–4, D 16–D 25 (SCHOTT) is well defined, and as the definition in Table T 10–5 shows, is relatively simple to measure and corresponds with a viscosity of 10^{8} P. In general, finding the absolute viscosity is far easier at higher temperatures, i.e. in the glass-blowing range, and also in the range of temperatures where factory products are blown or pressed. In glass-manufacturing circles, there is essential agreement on publishing the so-called "softening point" ($\eta = 10^{7.6}$ P)

[15] According to recent work ([2]LILLIE), the strain-point viscosity is not, as hitherto accepted, $10^{14.6}$ but $10^{14.5}$ P, and annealing point value is not $10^{13.4}$ but 10^{13} P. This is provided that the fiber method (see below) is used to measure viscosity in a range between a temperature about 25° above the annealing point and about 15° below, under conditions of falling temperature (4°/min) and the strain point is obtained by extrapolation from the viscosity values in the log η-temperature diagram.

[16] The strain point (e.g. Table T 10–4, A 1 of CORNING glasses) for ordinary silicate glasses lies at 25–40° below the transition temperature (T_g) (for high-quartz glasses, 70–80° lower), while the annealing point lies within $\pm 10°$ of the transition temperature.

[17] It is still the case, particularly with small-scale manufacturers, that the softening temperature is only the point at which a glass softens when judged by feel, and no precise figures are given; or the temperature may be given at which glass rod of some shape or other is clamped at one end in a horizontal position and bends after an unspecified time interval (see, e.g., Fig. B 10-13). Such data have only a very restricted significance.

and the so-called "working point" (10^4 P), which are values fully suited to the users of the glasses, in practice. On the other hand, the so-called "melting point" ($\eta = 10^2$ P) at which the viscosity is somewhat less than that of syrup at 25° [18] is of less interest



[10.2]

Fig. B 10-8 Measurement of viscosity by the fiber method

Fiber elongation Δl (lower curve) and furnace temperature T (upper curve) presented as time functions to determine the temperature for that viscosity which, under fixed fiber dimensions, heated lengths and loads, corresponds to an elongation rate of 1 mm/min. The temperature sought, $T_K = 934°$, lies on the upper curve perpendicularly above the intersection S of the lower curve with a tangent drawn parallel to the straight line of slope 1 mm/min and touching this curve

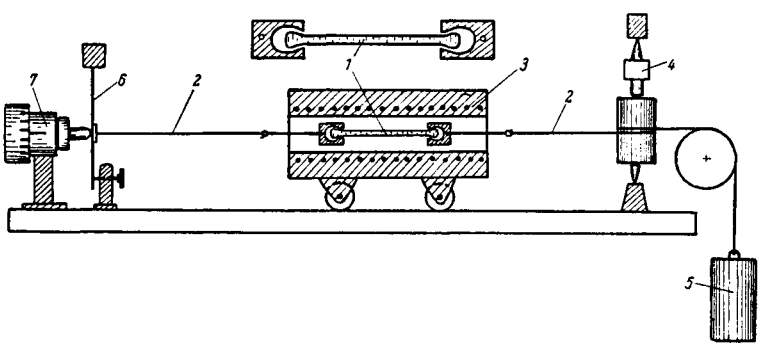


Fig. B 10-9 Apparatus for measurement of viscosity by the fiber method (elongation rate of a heated, loaded glass fiber) (from JENKEL)

1 fiber, 10–20 mm long, 0.1–0.4 mm dia.; *2* support and tensioning wires of nichrome; *3* movable furnace; *4* rotating axis with mirror to measure fiber elongation; *5* tensioning weight (*ca.* 1 kg/mm² of fiber cross-section; *6* brass leaf spring; *7* micrometer to calibrate the unit and set the zero

[18] In this range of the usual liquid solution, the glass melt contains only SiO_2 molecules and ions, e.g. Na^+, Ca^{++}, SiO_3^{--}, etc.

to the vacuum user than to the glassworks man, e.g. in the problem of fining a melt which depends on the rate of ascension of trapped gas bubbles in the furnace melt.

Measurement of glass viscosity η. Since the spread of viscosity values of technical glasses (silicates) includes twelve orders of magnitude, different methods are naturally necessary according to the range involved.

In the annealing range ($\eta = 10^{14.5}$ to 10^{13} P) the viscosity is usually found by the rate of elongation of a loaded and well-annealed fiber by means of the equation (LEWIS, [1]LILLIE):

[10.2]

$$\eta = \frac{981 \cdot G \cdot l}{3\,\pi r^2 \cdot \Delta l/\Delta t} \quad \text{(P)},\ ^{19}$$

where G(g) is the load, l (cm) the homogeneously heated gauge length of fiber, r (cm) the fiber radius (generally 0.3–1.0 mm) and $\Delta l/\Delta t$ (cm/sec) the rate of elongation at the temperature of measurement. Since the precision of measurement depends on the rate of heating in the furnace, it is recommended that the best rate be determined (somewhere between 5 and 10°/min). The curve in Fig. B 10-8 gives an example of the fiber method for determining viscosity, corresponding (for certain fiber dimensions and loads) to a rate of elongation of 1 mm/1 min, the heating rate having been chosen as 10°/min and the length read off every 30 sec. Figure B 10-9 shows a proven device for this method; see POOLE for the corresponding set up with vertical glass fiber suspension; Fig. B 10-10 gives a simple arrangement which allows rapid and qualitative investigations of η in the annealing range to be carried out by unskilled personnel.

The determination of the *strain* or *annealing point* must by definition (see Table T 10–5) employ photoelastic methods.[20] Figure B 10-11 shows the scheme. The artificially strained glass test-pieces (e.g. rods 5 mm dia. and 25 mm long) are placed in a carbon holder with a well-annealed standard glass rod of the same type of material whose strains are at most 10 mμ/cm. Both rods are then moved into the center of the furnace where the temperature is constant; sometimes they are preheated in the appropriate zone of the furnace to a temperature below the annealing range. After the test-piece has reached the constant temperature of the furnace center, the polarization unit is used to observe the time in which strains in this rod fall to the low level of the residual strains in the standard. If these measurements are repeated on a new sample of the

[19] A more convenient equation for calculation is the LEWIS expression:

$$\eta = 2.5\,\frac{l \cdot t_a \cdot G}{\Phi^2} \cdot 10^3 \quad \text{(P)};$$

l(cm) = heated length, Φ (mm) = diameter of glass rod, G (g) = load, t_a (min) = time needed to produce 1 mm increase in gauge length. If the surface of the fiber is introduced into the above expression by means of the volume which, unlike the diameter, remains constant during the measurement, and the equation is integrated ROBINSON shows that one gets the following very useful form:

$$\eta = 19{,}600\,\frac{G}{V} \cdot \frac{l_0 \cdot l_1}{l_1 - l_0}\,(t_1 - t_0) \quad \text{(P)},$$

where G is as before, V (cm^3) = the fiber volume, l_0 (cm) the heated length at time t_0, and l_1 (cm) the length at t_1, while $t_1 - t_0$ (min) is the time-interval between two length measurements.

[20] See 10.3.IX for further details on stress (strain) measurements in glass.

same material equally strained at a second furnace temperature, one observes that the time needed for annealing, t_e, is a falling exponential function of annealing temperature T_e, that is

$$t_e = a\, e^{-kT_e} \quad \text{or} \quad \log t_e = b - kT_e,$$

where k, a and b are constants. The two measured values may be joined by a straight line on semi-logarithmic paper (see Fig. B 10-12); from this, extrapolation will deter-

[10.2]

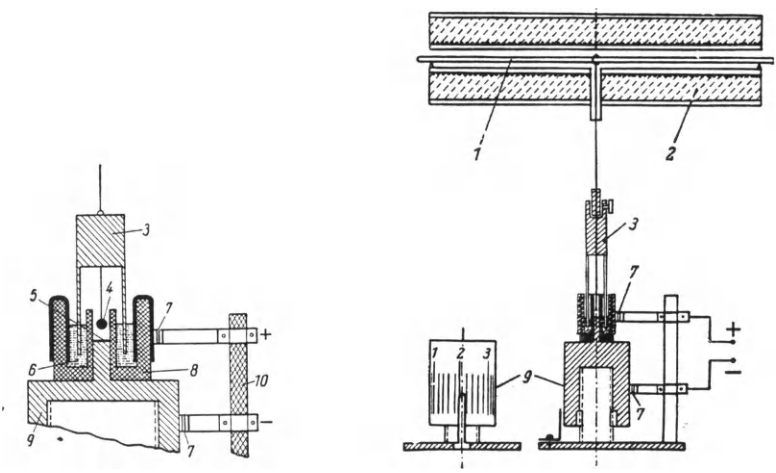


Fig. B 10-10 Apparatus for determination of relative viscosity in the annealing range by the bending method ([4]GEHLHOFF)

1 glass rod (230 mm long, dia. standardized arbitrarily) laid on two knife-edges; *2* horizontal furnace; *3* load, large compared with the weight of the rod (160 g); *4* Ni-plated brass contact ball; *5* Pt contact to indicate a predetermined fall of *3*; *6* annular Hg-pool current-conductor; *7* sliding contact; *8* hard-rubber pot; *9* micrometer height-setting control for Pt contact to fix desired maximum drop and for calibration; *10* insulating support for the slide contact. Procedure: (a) set a fixed gap between *4* and *5* (max. drop for *3*), e.g. 3 mm; (h) heat 2 at fixed rate (e.g. 4°/min); (c) measure temperature of furnace at the moment when, say, an alarm bell indicates electrical contact between *4* and *5*

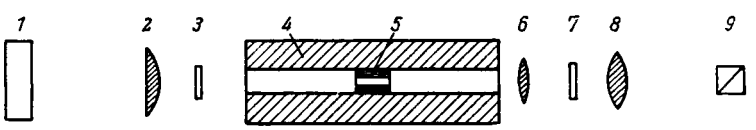


Fig. B 10-11 Schematic view of equipment to measure stress-relief temperatures T_{str} or T_{an} ([2]DALE)

1 Hg lamp, 250 W, in housing; *2* plano-convex condenser lens 100 mm dia., 175 mm focal length; *3* polaroid filter; *4* furnace; *5* carbon block with glass test-piece, standard glass rod and PtRh-Pt thermel; *6* biconvex objective (40 mm dia., 75 mm focal length); *7* Wratten filter 77A; *8* biconvex collector lens (100 mm dia., 175 mm focal length); *9* analyzer (cf. also 10.3.IX)

mine the 15 hr (T_{str}) and the 15 min (T_{an}) points, or any other such values, quite easily. Figure B 10-12A shows a similar unit for quantitatively following the reduction in strain as a function of time of heating at constant temperature. Figure B 10-12B shows a curve obtained with this apparatus, and the strain and annealing points can be found with greater precision by its means.

The measurement of viscosity in the central range, which is involved in flame-working, is mostly performed by the fiber method described above. Here, however, no

special weight is used, and elongation takes place under the specimen's own weight. The practice is to use test rods of 0.5–1 mm dia. and 30–50 cm length whose upper end is heated at 5–8°/min over about 10 cm. For comparative tests, a very suitable device is shown in Fig. B 10-13. One end of a glass rod is fixed and the other is heated

[10.2]

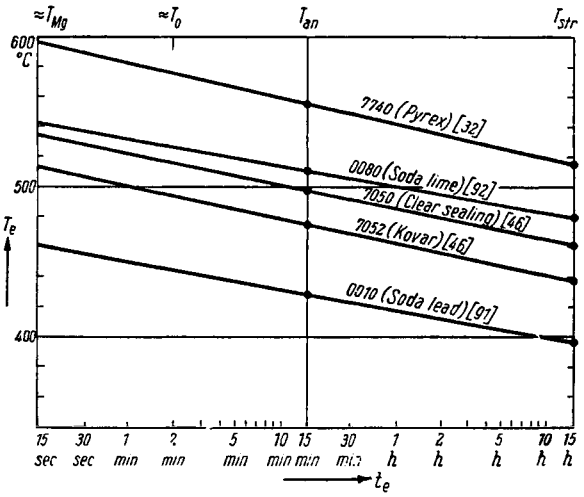


Fig. B 10-12 Annealing temperature T_e (linear) of some CORNING glasses as a function of corresponding annealing time t_e (logarithmic)

The curves are linear to within measurement accuracy. The characteristic annealing points T_{str} (15 hr), T_{an} (15 min) and T_0 (2 min stress-relief temp.) are easily found by extrapolation through two arbitrary points on the lines. Numbers in [ ] are expansion coefficients in units of 10^{-7}/°C

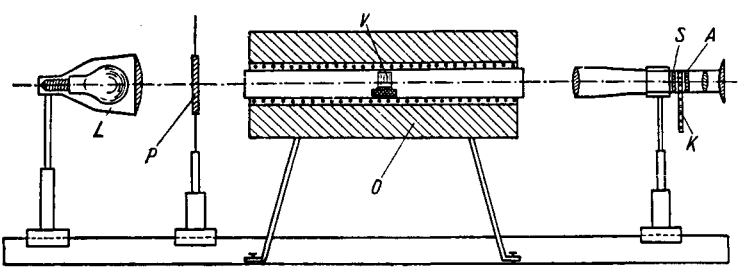


Fig. B 10-12A Arrangement for following quantitatively the stress-relieving of an artificially strained glass test-piece as isothermal heating proceeds (SCHILL)

L light source; *P* polarizer; *O* furnace; *V* strained glass test-piece (cylinder 20 mm dia., 20 mm long with polished faces on a quartz-glass protection tube); *S* delay disk to produce path difference of 520 mμ; *K* removable compensator; *A* analyzer (details in 10.3.IX)

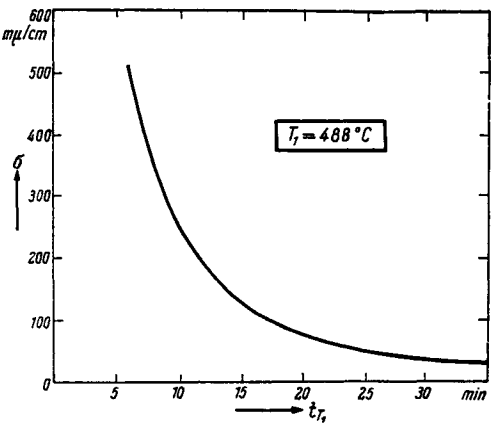
in a furnace. The temperature is found at which the unsupported end drops at 1 mm/min per effective gram of glass; by the therm "effective wegiht" one means the product of length l from the center of the furnace to the end of the rod × cross-section of rod × density of the glass.

In the liquid range of viscosities of importance for glass furnace work, i. e. at elevated temperatures (η = ca. 10^5 — 10^1 P), the viscosity is determined by the speed of rotation

of a stirrer in the melt (see Fig. B 10-14). η is given by

$$\eta = \frac{981 \cdot R \cdot Q \cdot t_u}{2\pi^2 (L + \delta)} \left(\frac{1}{d_1^2} - \frac{1}{d_2^2} \right) \quad \text{(P)},$$

where R (cm) = radius of the graduated measuring disk, Q (g) = weight that actuates the disk's perimeter, t_u (sec) = time of one revolution of the disk, L (cm) = length of



[10.2]

Fig. B 10-12B Decrease in stress σ in a glass test-piece heated at constant temperature T_1 as a function of heating time t_{T_1}, measured by unit shown in Fig. B 10-12A

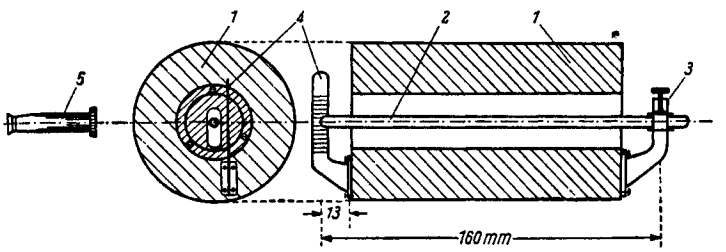


Fig. B 10-13 Apparatus for plant control of glass viscosity in the middle range of values, by comparative testing (see also [1]ENGLISH)
1 furnace; *2* test rod supported at one end; *3* support; *4* scale; *5* telescope to measure rate of fall of rod tip

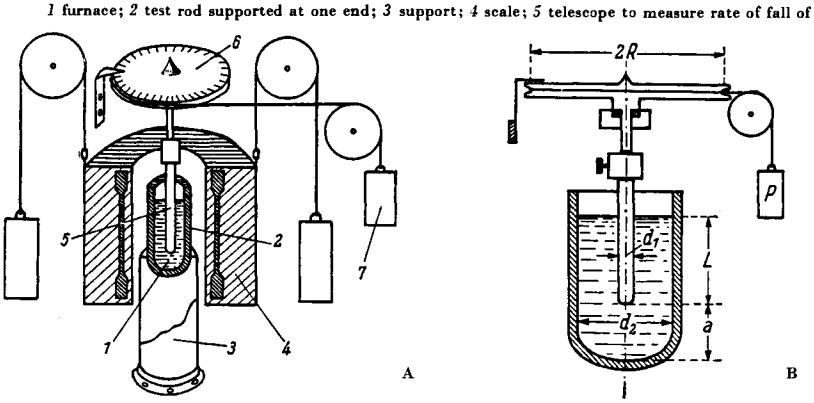


Fig. B 10-14 Stirrer viscosimeter for determination of viscosity of liquid glass (CROOK)
1 glass melt; *2* cylindrical sillimanite pot, I.D. = d_2; *3* holder socket for *2*; *4* drop-over furnace with Silit heater rods, up to 1400°; *5* cylinder stirring rod (dia. = d_1) of sillimanite; *6* graduated wheel and pointer; *7* weight *P* which engages the wheel perimeter by means of wire fed over a pulley; *L* length immersed; *a* distance between end of rod and floor of melt

the rod immersed, δ = correction term which takes account of the distance a of the rod from the floor of the melt,[21] d_1 (cm) = diameter of rod stirrer, d_2 (cm) = internal diameter of outer cylinder which contains the glass.[22]

Viscosity in the fluid region can also be found by the rate of fall of a Pt ball. The position of the ball can be determined either by X-rays displayed on a screen or by H.F. induction coil, inductance being a maximum when the ball traverses the coil. Another way is to use the so-called "ball drag viscosimeter"; here is measured the rate at which a Pt ball, suspended on a Pt wire at the bottom of the melt, is drawn out of the melt by a heavier weight via a roller (MÜLLENSIEFEN), or by a beam balance (TIELSCH).

[10.2]

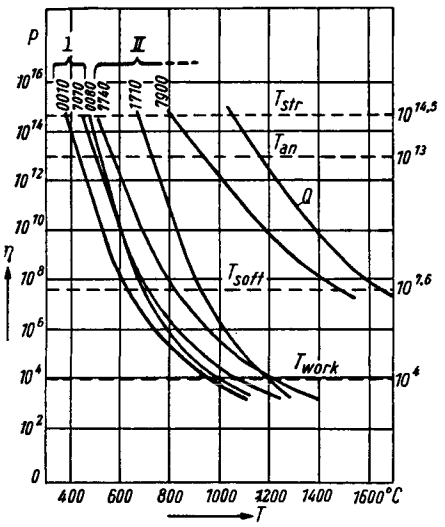


Fig. B 10-15 Viscosity η of CORNING glasses as a function of temperature T ([1]CORNING)
I soft glasses; *II* hard glasses; *Q* quartz glass

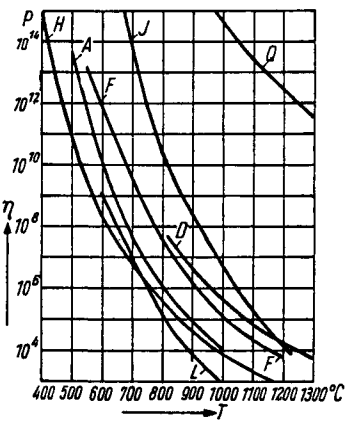


Fig. B 10-16 Viscosity η (from [1]DOUGLAS) as a function of temperature T (for compositions see Table T 10-2, E 4), *Q* quartz glass

In all measurements of glass viscosity at elevated temperatures, not only is it of fundamental importance to try for constant, homogeneous and precisely determined heating of the whole glass mass, but one should also watch for sublimation of glass components and for devitrification phenomena and where possible prevent them.

Figures B 10-15 and B 10-16 give a few measurements on η of technical glasses as temperature functions. The curves can be represented over a fairly wide range of temperatures by

$$\eta = Ae^{b/T} = Ae^{B/RT}; \quad \text{or} \quad \log\eta = \log A + b\,(1/T),$$

where η (P) = viscosity, T (°K) = temperature, A (P) and b (°K) are constants, B (cal/mol.) = activation energy, R = 1.99 cal/mol. deg, the gas constant. This shows that the values of η when plotted logarithmically against $1/T$ lie on a straight line if B remains constant. Figures B 10-18 to B 10-20 show measurements plotted in this way,

[21] For $a > 1$ cm, δ can be neglected; at 0.3–0.7 cm, δ = 0.03 cm.
[22] See [1]ONDRÁČEK for a modified apparatus based on this principle.

and in fact are almost linear over the range 10^{13} to 10^{9} P; Fig. B 10-17, obtained for a glass between 10^{2} and 10^{14} P, shows that linearity, and therefore constant activation energy, only exists over a limited temperature range (cf. also [21]ANON. and supplementary material at the end of the book). The temperature (°K) dependence of viscosity is still better expressed by the equation (FULCHER)

$$\log \eta = a + (b/T - T_0),$$

where η is the viscosity (P), and a, b and T_0 are constants. Extensive measurements by the Committee of the Society of Glass Technicians (England) (*J. Soc. Glass Tech.* **40** (1956) 83*P*–104*P*) gave for a soda-lime glass (I): [10.2]

$$\log \eta = -1.648 + \frac{4522}{T - 242}$$

and for a borosilicate glass (II)

$$\log \eta = -0.772 + \frac{4635}{T - 242}.$$

The glass compositions were:

GLASS	w/o COMPOSITION									
	SiO_2	B_2O_3	Al^2O_3	Na_2O	K_2O	MgO	CaO	TiO_2	Fe_2O_3	Cl
I	72.76	–	1.36	12.86	0.67	3.81	8.11	0.049	0.186	–
II	80.04	13.20	2.07	4.12	0.24	–	–	0.036	0.061	trace

With regard to the influence of glass composition on viscosity, alkali, especially Na_2O, markedly lowers η (see, e.g., Fig. B 10-21). Similarly, η fails with rising Al_2O_3, BaO and PbO content, and also with B_2O_3 content but only up to 15% ([4]GEHLHOFF). See OCHOTIN on the determination of viscosity of soda-lime glasses with varying Na_2O, CaO, Al_2O_3 and MgO contents from nomograms.

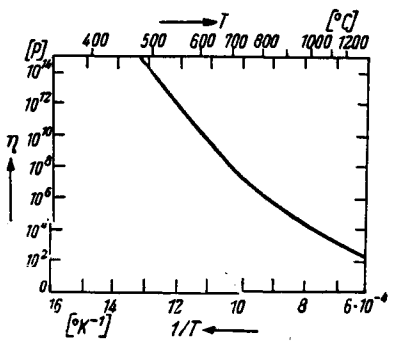


Fig. B 10-17 Viscosity η of a technical glass (log scale) against $1/T$ ([2]PRESTON)
In the range 10^{13} to 10^{8} P, the curve is almost linear

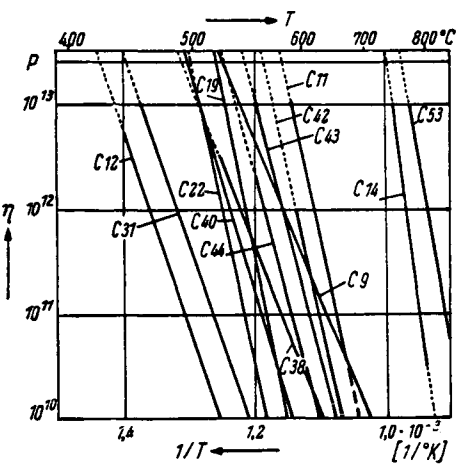


Fig. B 10-18 Viscosity η of BTH glasses (see Tables T 10-2 and 10-4, E 1) plotted logarithmically against $1/T$
In the range $10^{13.6}$ (T_{an}) to 10^{10} P, each curve is linear

From the position and slope of the viscosity-temperature function the following characteristics can be deduced: if the annealing point lies in the relatively low-temperature range (*ca.* 380–450°, see Fig. B 10-15, Group I), the glass is called soft, while

10.2]

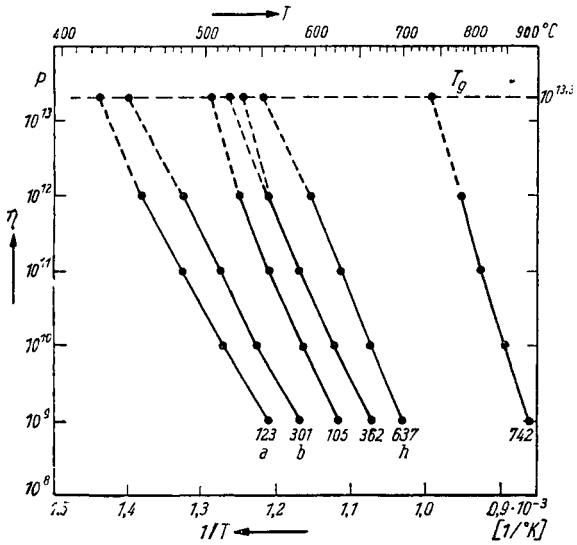


Fig. B 10-19 Viscosity η of OSRAM glasses as functions of $1/T$ (from OSRAM). Cf. also Table T 10–4, D 8

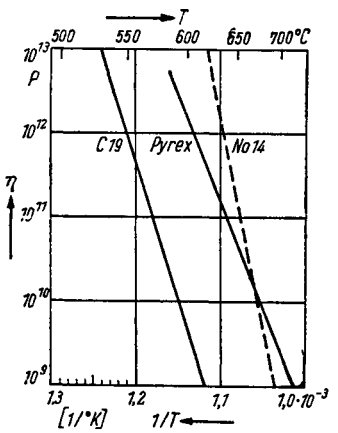


Fig. B 10-20 Viscosity η of a phosphate glass Type No. 14 (from [3]STANWORTH), as a function of reciprocal temperature $1/T$

In the range 10^{12} to 10^{9} P, practically linear, as are the silicate glasses 7740 Pyrex (CORNING) and C19 (BRITISH THOMSON-HOUSTON)

glasses with T_{an} between 450 and 500° are medium hard, and those over 500° (see Fig. B 10-15, Group II) are called hard. If the range of the viscous state (in so far as flame-working the glass is concerned, 10^8 to 10^4 P) extends over a wide range of temperature, the glass is called "long". Fall-off of viscosity with rising temperature is quite gradual in such a glass, which is therefore very suitable for hand working in the torch flame, since the temperature does not have to be adjusted so precisely. On the other hand, glasses whose working-range viscosity drop is very steep soften very quickly as temperature rises, and solidify very rapidly when it falls; these are known as "short". Short glass is best suited to glass-working machinery where exact temperatures are possible in the heating period, and where relatively short operational times have to be reckoned with. Quantitative indices of the length or shortness of a glass can be found by data on the temperature range in which the viscosity falls from 10^8 to 10^4 P.

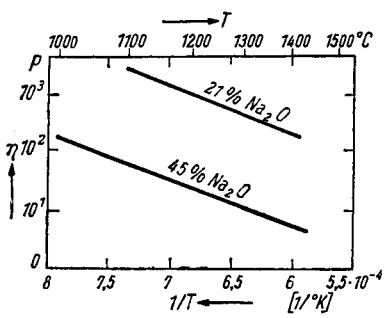


Fig. B 10-21 Viscosity of two sodium-silicate glasses (21 and 45% Na_2O) as functions of temperature T ([2]PRESTON)

10.2.III. *Devitrification*

Closely associated with viscosity is the "devitrification" of a glass, which has been mentioned several times before. Since glass, as a supercooled liquid, is thermodynamically unstable, it tends to crystallize out if held for long enough in a suitable range of temperature. Below this range, the viscosity is so low and hence the diffusion so small that no crystals can grow, and above it, crystals that have formed may dissolve in the melt again, and therefore the crystal formation rate is maximal in this region (see [10.2]

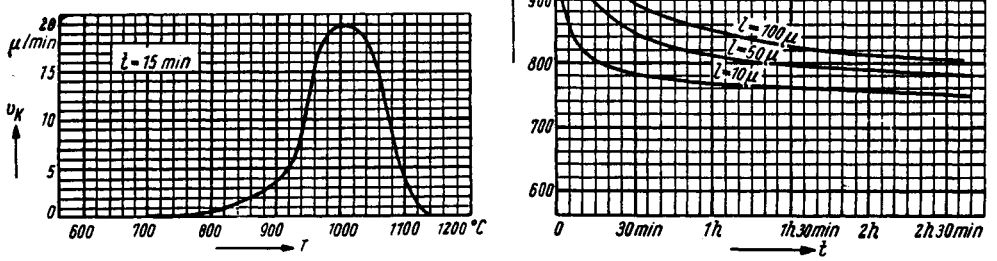


Fig. B 10-22 (*Right*) Curves of equal crystal-growth length l in the temperature (T)time (t) diagram (from [1]GEHLHOFF). (*Left*) Crystallization rate v_K, taken from the 15 min heating time ordinate of the right-hand figure, as a temperature (T) function

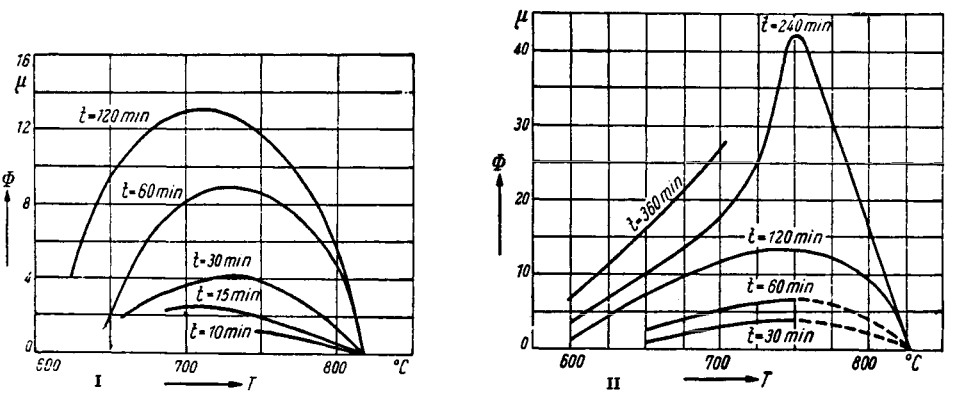


Fig. B 10-22A Size Φ of crystals produced by devitrification, as temperature (T) functions, for different heating periods t (from [3]KNAPP). (Cf. also Table T 10–5A)
I magnesia bulb-glass; II lead oxide foot-glass

Fig. B 10-22). However, the devitrification temperature, so-called, does not usually mean the point at which this maximum occurs, but that at which, after prolonged heating, the first traces of small crystals occur in the originally clear glass and can become so numerous that the glass finally turns opaque. The critical range in which this can happen, and through which heating and cooling processes are taken as rapidly as possible, lies according to the type of glass between temperatures at which the vis-

cosity is about 10^7 to 10^3 P. Generally, any glass can be devitrified if it is held long enough in the appropriate temperature range, but the tendency to devitrify depends very much on composition. The tendency is usually less the more components make up the glass. For example, the alumina content of Thüringer glasses greatly reduces the tendency to devitrify; this was originally due to the composition of the local quartz sand, or was achieved by putting furnace brick containing clay in the glass melt.

It is clear that for technical purposes the most important glasses are those whose tendency to crystallization is least, so that even with prolonged working in the critical [10.2] viscosity range and during subsequent thermal treatment, no detectable devitrification occurs. Figure B 10-22 A shows the size of the crystals for various heating intervals and temperatures for two glasses of great importance to vacuum work, a magnesia bulb-glass and a lead foot-glass. Table T 10–5 A gives characteristic devitrification data derived from these curves.

TABLE T 10–5 A. CHARACTERISTIC DEVITRIFICATION DATA FOR TWO TYPES OF GLASS ([3]KNAPP)

PROPERTY		MAGNESIA BULB-GLASS(1)	LEAD FOOT-GLASS(1)
Lowest temperature at which devitrification is just visible	°C	600	600
Liquidus temperature, above which no crystalization is possible	°C	820	830
Temperature of maximum crystal growth rate	°C	700–720	750
Max. crystal growth rate (crystal size/time)	μ/min	0.16	0.18
Max. size of crystal found (cf. Fig. B 10-22 A)	μ	16.6	43.0
Shortest time in which crystals appear which are visible under the microscope	min	*ca.* 10	*ca.* 30

(1) Composition:

		SiO_2	PbO	Al_2O_3	Na_2O	K_2O	CaO	MgO	BaO
Magnesia glass	%	70.3	–	1.4	16.4	1.0	5.5	3.4	2.0
Lead glass	%	55.2	32.2	–	4.3	8.3	–	–	–

10.2.IV. *Thermal Expansion*

This parameter plays a large part in tube manufacture, because on it depends the feasibility of making durable seals, e.g. of bulb-glass to foot-glass, from different types of glass, and vacuum-tight joints between glass and metal.

The thermal expansion, as is well known, is determined in the dilatometer by taking the expansion or contraction curve $\Delta l/l_0 = f(T)$, that is by measuring the relative change in length of a rod (in the same length units) when it is heated or cooled. These characteristics are reversible up to near the deformation point. The gradient gives the length change per °C or the so-called true thermal expansion,

$$\alpha = dl/l_0\, dT \quad (\text{mm/mm °C}) .$$

Since the expansion curves of glasses, even below the transformation range, are not strictly linear, but increase with temperature at a rate greater than the linear one, which

means that α steadily increases a little also, it is usual to calculate the *mean* coefficient,

$$\alpha_m = \Delta l / l_0 \Delta T$$

for a given temperature range ΔT. In general, the $\alpha(20 - T_g)$ between 20° and the annealing point for technical glasses is about 5–20% higher than α (20–100), taken from 20° to 100°; it is about 1–3% higher than the α (20–300) value, taken from 20° to 300°. Many manufacturers therefore settle for the 20–300 range coefficient and the transition temperature (OSRAM) or annealing point (CORNING) when publishing data. Others give the whole expansion curve for their commercial glasses, which is preferable, [10.2] and they guarantee a definite tolerance on α (e.g. CHANCE, G.E.C., see Table T 10–4, E 2: GSD and GWD glass).

If two glasses are joined when heated, and do not contract in the same way, i.e. have different α s, then they will stay reliably joined so long as one or both remain above the stress-relieving temperature; while *one* partner is still plastic, no mechanical stresses can build up as a result of their different contractions. But as soon as both are cooled to below the lower of the two annealing temperatures, i.e. both are brittle, the different contractions will give rise to mechanical stress, since the glass with the larger thermal expansion will contract more than its partner when cooled. Once a certain degree of stress is exceeded, the boundary or joint will crack. It follows from these considerations that stresses which arise from expansion differences cannot be removed by any length of annealing period and slow cooling, as they always form below the stress-relieving temperature range. These stresses can be observed as strains in the polarizer strain-viewer (see below) which can measure them quantitatively; in soft glasses, experience has shown that they remain below the breaking stress if the average α s (between room temperature and the annealing point of the glass of lower softening point) of both glasses do not differ by more than 10%, if their transition temperatures are not too different and if both glasses dissolve well in each other.

If two glasses cannot be joined directly because their expansion difference is too large, intermediate glasses have to be used; a whole series of these is available commercially, with α s between 14 and 114×10^{-7}l/°C (see Table T 10–4). With their aid, graded seals between one glass and another are possible without exceeding the highest permissible stress at any one of the joints.

The behavior of glass-metal seals is far more complex; the permissible difference between mean α s (measured between room temperature and the "setting point") depends on the shape of the seal, the plasticity of the metal and tempering and annealing schedule after making the seal. See Chapter 30 for details.

To achieve satisfactory control of all these processes, it is not enough, as it formerly was simply to know the average α (20–100°), the figure that was often the only one given by the manufacturer; it is recommended that the whole expansion curve be obtained particularly in the region of the deformation point, when more precise investigations are involved (especially for sealing-glasses).

When the transition temperature or the annealing point is approached, as already stated (see Fig. B 10-7), the expansion curve begins to show a steeper slope; this phenomenon is explained by the variation not only of the ordinary intermolecular distance but also of the degree of aggregation of the glass particles above T_g, whereas

below T_g only the molecular gaps vary. However, in general, this is only of interest up to the quick annealing point ($\eta = ca.\ 10^{13}$ P), since above this the viscosity is low enough to prevent stress formation even with partners whose expansions are quite different.

In the measurement of the thermal expansion of glasses, it should be noted that, since the thermal conductivity is poor, temperature changes should not be carried out too quickly if it is desired to heat the sample evenly. The maximum rate in practice is 1–4°/min [23] (KLEMM); care should be taken also to anneal the samples properly, since only well-annealed glasses subject to modest temperature rises will show reproducible

[10.2]

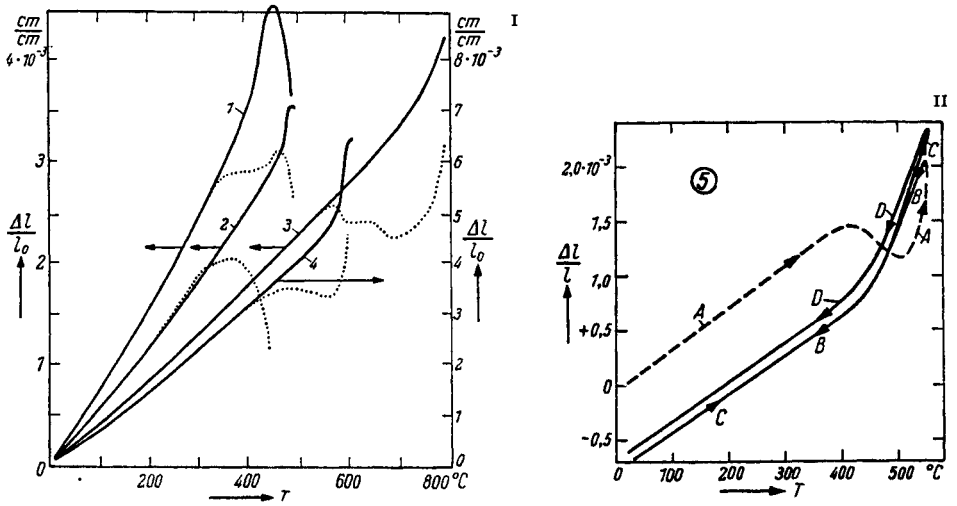


Fig. B 10-22B Expansion curves of annealed (———) and unannealed (.....) glasses: relative expansion $\Delta l/l_{20}$ as temperature (T) function (Δl = expansion, l_{20} = gauge length at 20°) *1* PHILIPS glass 111; *2* borate glass according to [2]DALE; *3* hard glass according to [3]DOUGLAS; *4* hard glass according to [1]TURNER*; *5* CORNING glass 7720 (Nonex), *A* not annealed, *B* and *C* contraction and expansion curves after 2 hr anneal in dilatometer, *D* contraction after second 2 hr anneal at 550° (TOOL)

* Composition: 56.8% SiO_2, 19.4% B_2O_3, 0.9% Al_2O_3, 7.4% Na_2O, 7.1% K_2O, 8.5% CaO, 0.1% Fe_2O_3.

and reversible characteristics. Poorly annealed and strained glass has a somewhat higher α (*ca.* 2%) than glass[24] which has been annealed at sufficiently high temperatures and well annealed, and the expansion curve of highly strained glass that is heated up in the dilatometer near the stress-relieving range (transformation region) will show irreversible irregularities (see Fig. B 10-22B). In this case, the expansion coefficient is found by taking only the contraction curve after heating the sample at a high enough temperature and may be checked by heating the testpiece again in the dilatometer to see that the resultant expansion curve (rising temp.) agrees with the contraction curve (falling temp.) for the same temperature–time variations, or at least has the same slope. It should also be noted that prolonged expansion tests and tempering processes can lead to chemical changes in glass composition, for example by evaporation of alkalis, which may cause variations in the expansion characteristics ([6]ESPE).

[23] It takes at least 8 hours to record a complete expansion and contraction characteristic between 20° and 500° at the standard temperature rise of 2°/min.

[24] See 10.3.VIII for annealing processes.

Methods for determination of the expansion coefficient α of glass. The usual method is to employ a quartz dilatometer which determines the thermal expansion of a test sample relative to that of quartz. To the values so obtained one must add the expansion coefficient of quartz (see Table T 11–3) to find the absolute value of α. Figure B 10-23 shows a relatively simple dilatometer in section and overall view, by means of which, with an oil bath, expansions up to *ca.* 200° can be made, and with a slide-over electric furnace,[25] up to *ca.* 600°. The expansion of the sample A under test is found from the change of angle between two reflecting prisms P_1 and P_2 by an autocollimating telescope.[26] The [10.2]

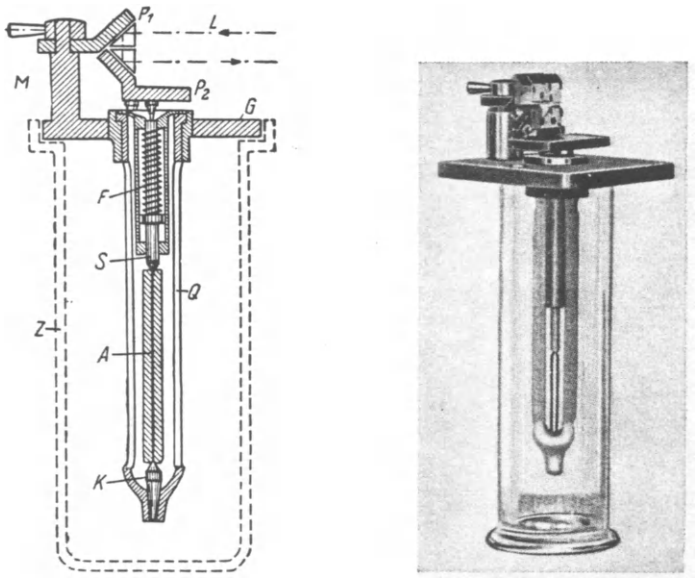


Fig. B 10-23 Cross-sectional and overall views of a quartz dilatometer for measuring the expansion coefficient of materials in rod form in a heated oil bath up to 150° (made by SENDLINGER OPTISCHE GLASWERKE, GOERZ A.G.)

A test-rod; *K* and *S* pointed quartz-glass rods; *Q* quartz tube; *G* base-plate; P_2 movable tripod table with total-reflexion prism, with 2 feet on plate *G* and 1 foot on rod *S*; P_1 total-reflexion prism, fixed position, held by stand *M*; *L* pencil light-beam for observation of prism table P_2; *Z* heatable oil bath or furnace (see BRAUN for further details)

precision is 0.5–1%. A dilatometer constructed on the same principles for work up to 1000° is shown in Fig. B 10-24. In addition, self-recording dilatometers are available, like the BOLLENRATH photographic recording unit made by LEITZ, Wetzlar (Fig. B 10-25), the CHEVENARD dilatometer (Fig. B 10-25A), which uses mechanical recording and ink-pen (also supplied recently with photographic plotting) and a new design by ULBRICHT (Fig. B 10-25B), specially suitable for continuous production measurements. For American equipment see, for example, HIDNERT, KINGSTON, SYLVANIA ELECTRIC

[25] With a central Cu cylinder, closed along the bottom, and with base-plate *G* cooled by an interlayer flushed with water.

[26] The expansion can be determined accurately enough with a dial gauge (sensitivity 1 μ per scale division) if the constant temperature zone in the dilatometer is at least 10 cm long and the dial gauge is protected against thermal radiation by a water-cooled flange (see, e.g., HÄNLEIN for further details).

PRODUCTS. The mechanically recording instruments are certainly not so accurate, but they possess the advantage of greater simplicity and speed of operation. It is also possible to determine the expansion of the rod in dilatometer testing by measuring and electric-

[10.2]

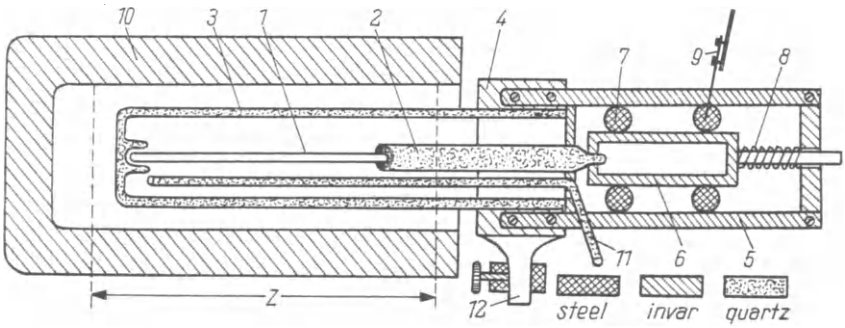


Fig. B 10-24 Dilatometer for expansion measurements up to 1000° ([6]ESPE)

1 test-rod; *2* sheathing and supporting rod of quartz glass; *3* quartz tube; *4* Invar support for tube *3*; *5* Invar bracket; *6* carrier of square Invar rods, running on steel cylinders *7*; *8* compression spring to force carrier *6* against the test-piece *1*; *9* mirror attached to axis of bearing cylinder to indicate movement of carrier *6* due to expansion of test-rod *1*; *10* removable tube-furnace; *11* protective gas inlet; *12* holder, adjustable in height; *Z* even-temperature zone in furnace

ally recording the capacitance between an electrode fixed to the rod and a fixed electrode. SYLVANIA ELECTRIC PRODUCTS (Electronics Div., New York 18) have marketed a fully automatic electronically controlled model with facilities for pre-set temperature-

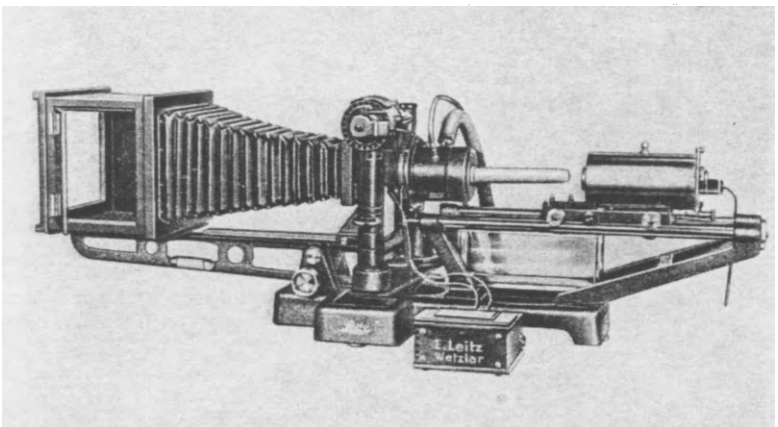


Fig. B 10-25 Differential dilatometer (BOLLENRATH) made by the ERNST LEITZ optical company, Wetzlar, Western Germany, with photographic recording

Recording area 240 × 240 mm; magnification of the expansion of the 50 mm gauge length is standard at 200×, but an optical magnification system can raise this to 400 and 800×; max. temperature 1100°; only 12 g pressure on the sample; an additional unit (micrometer with optical adjustment) is needed for calibration; by means of a tensioned ribbon-mirror galvanometer inserted in the recording lightbeam, and operated by a thermel in the furnace, the absolute expansion curve (no comparison sample) can be taken

time programs up to 1000° and pen-recording output. See TURNBULL for a piezo-electric design.

A very convenient set-up, especially for testing glass-metal pairs for making seals is as follows: no comparison of each member separately with quartz is made, but both

are compared directly with each other in the dilatometer; the comparison tube of quartz (No. 3 in Fig. B 10-24) is replaced by one of the same shape in the glass concerned. For a given temperature, the optical indicator gives directly the difference in expansion between the two partners. Figure B 10-26 shows examples of a few curves

[10.2]

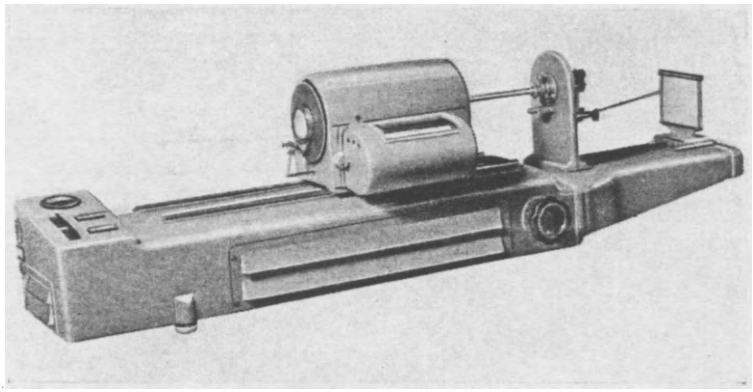


Fig. B 10-25A CHEVENARD differential dilatometer with mechanical curve plotter (sold by ALFRED I AMSLER, Schaffhausen, Switzerland)

Ordinate 6 mm per μ expansion, abscissa 62 mm for 0–1000°. A higher sensitivity model can be supplied using an optical curve plotter

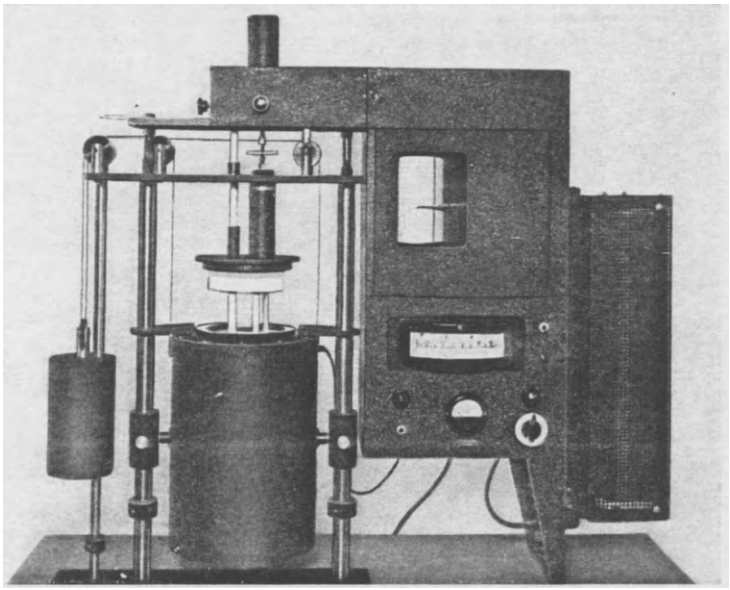


Fig. B 10-25B Differential dilatometer (ULBRICHT) with mechanical inked-drum recorder (6.6 hr/rev.) (made by K. ULBRICHT, Haldensleben, Eastern Germany)

Maximum height of ordinate ($\Delta l/l_{20}$ axis) = 160 mm; test-piece = 65 mm, switched magnification of expansion = 200 or 400 ×; temperature read off the thermocouple meter at various times and marked on the drum electromagnetically by hand-operated switch, max. temperature 1200°; recording drum perimeter 340 mm; temperature-axis length as desired since recording is possible over many drum revolutions

taken by this method on different glasses against 26% CrFe. This process is also suitable for continuous quality control of new supplies of glass by comparing them with a standard type.

A simple works test for qualitative comparison of the expansion of two types of glass is the so-called "snap-ring method". A ring of a known glass I is fitted with a ring of the second glass under test A round the periphery; they are well annealed and slowly cooled. After slitting the double ring along a line perpendicular to the periphery, the

[10.2]

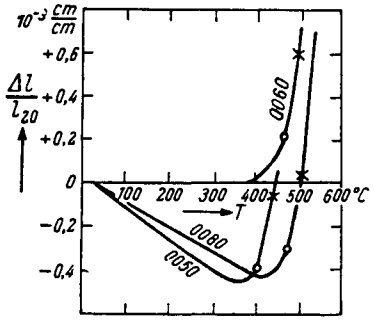


Fig. B 10-26

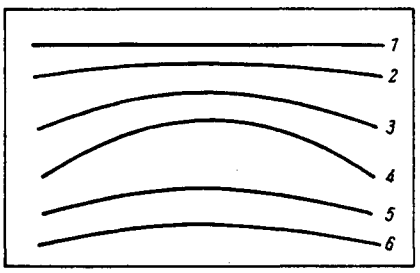


Fig. B 10-26A

Fig. B 10-26 Differential expansions $\Delta l/l_{20}$ of three technical CORNING glasses against CrFe (26/74) as temperature (T) functions, made in a dilatometer with free expansion of the glasses and the comparison metal (E. E. BURGER, [1]HULL)

○ 15 hr annealing temperature (strain point);
× 15 min annealing temperature (annealing point)

Fig. B 10-26A Approximate curvatures of twin glass fibers made of different pairs of glasses for comparative tests on expansion coefficients α (units of 10^{-7}/°C):

GLASS NO.	GLASS TYPE 1	α	GLASS TYPE 2	α
1	Corning 7740 (Pyrex)	33	Corning 7740 (Pyrex)	33
2			Corning 7720 (Nonex)	36
3			Corning 3320 (Uranium)	41
4			Libbey-Owens L 650	47
5	Corning 7720 (Nonex)	36		
6	Corning 3320 (Uranium)	41		

test-piece behaves like a bimetallic strip. If glass A on the outside has a larger α than the one inside I, A contracts more than I on cooling and the snap-ring or ci-clip will close. In the reverse case, the two slits of the rings will tend to open. A more precise method is the so-called twin-fiber method. In this case, a rod of the unknown type of glass and one of the standard glass are fused together along their edges so that excess mutual diffusion of glass does not occur. The resulting glass piece is then evenly heated and drawn out to a thin "biglass fiber" or twin glass fiber. When cool, this is laid on a smooth flat surface and its curvature measured. With care, one should be able to detect expansion differences of as little as 1×10^{-7} cm/cm °C (ZUNICK). Figure B 10-26A shows the approximate curvature of a few biglass fibers made of various pairs of glasses.

The linear expansion coefficient of a technical glass between 0–100° can be roughly computed from its n components as

$$\alpha = \sum_{i=1}^{i=n} \alpha_i p_i \quad (1/°C),$$

where p_i is the weight per cent of the i^{th} component and α_i the expansion coefficient of the same component (oxide), as given in Table T 10–6.

TABLE T 10–6. CONSTANTS (a) FOR CALCULATION OF LINEAR THERMAL EXPANSION COEFFICIENTS α (0–100) OF A TECHNICAL GLASS FROM THE WEIGHTS PER CENT (p) OF ITS COMPONENTS[1] [10.2]

I. WINKELMANN and SCHOTT (see FRANK)

$3\alpha = (a_1 p_1 + a_2 p_2 + \cdots + a_n p_n) \cdot 10^{-7}$ (1/°C)

COMPONENT	a	COMPONENT	a	COMPONENT	a
SiO_2	0.8	Al_2O_3	5	CaO	5
B_2O_3	0.1	Na_2O	10	BaO	3

II. [2]ENGLISH

$\alpha_{0-100} = (a_1 p_1 + a_2 p_2 + \cdots + a_n p_n) \cdot 10^{-8}$ (1/°C)

COMPONENT	a	COMPONENT	a	COMPONENT	a
SiO_2	0.50	Na_2O	41.6	BaO	14.0
B_2O_3 [2]	−6.53	K_2O	39.0	ZnO	7.0
PbO	10.6	MgO	4.5		
Al_2O_3	1.4	CaO	16.3		

[1] For a new series see TAKAHASHI.
[2] Holds for 0–12% B_2O_3 only.

Figure B 10-27 shows corresponding results of systematic measurements on sodium silicate glasses with a fixed 18% of Na_2O, and where the SiO_2 content is increasingly replaced by another oxide, thus exhibiting the effects of the various oxides on expansion coefficient. Figure B 10-28 shows the strong influence of alkali content (measured on silicate glasses with PbO content) on the expansion coefficient.

Figures B 10-29 to B 10-39 give a series of expansion characteristics of technical glasses. Others, particularly for glass-metal seals, are to be found in Chapter 30.

For many glasses, the higher the softening point the lower the value of α, and vice versa. Very soft glasses with annealing temperatures between 380° and 450° have αs between 85 and 110×10^{-7}, while hard glasses with T_{an} above 500° have αs between 30 and 50×10^{-7} (1/°C). Kovar glasses are exceptional, e.g. OSRAM 756 b or CORNING 7052 with T_{an} *ca.* 475° and α (20–300) *ca.* 46×10^{-7} (1/°C). The lowest expansion coefficient of all technical glasses is that of quartz, whose α (20–600) is about 6×10^{-7}; the highest of the technical glasses for sealing to Fe is $113–128 \times 10^{-7}$ (1/°C). Figure B 10-40 gives a survey of magnitude and position of the ranges of expansion coefficients of glasses compared with some metals, ceramics and plastics.

[10.2]

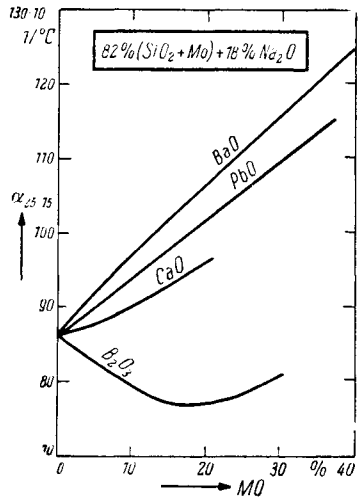


Fig. B 10-27 Average expansion coefficient α (25–75) of sodium-silicate glasses with fixed (18%) amount of Na_2O as a function of content MO of various oxides ([1]GEHLHOFF)

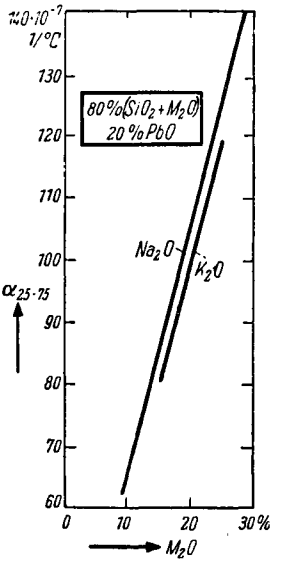


Fig. B 10-28 Average expansion coefficient α (25–75) of lead glasses (20% PbO) as a function of alkali content M_2O ([1]GEHLHOFF)

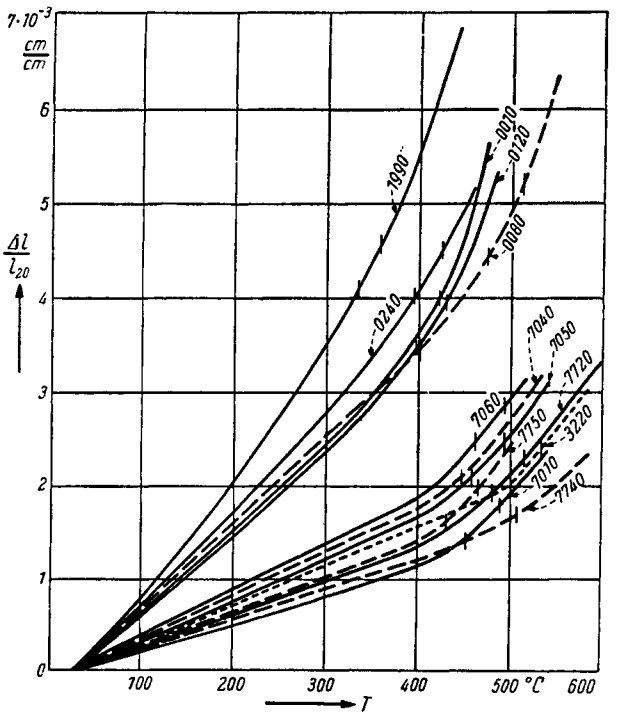


Fig. B 10-29 Expansion curves for the chief CORNING glasses (PASK)

The vertical lines in the curves mark the limits of the annealing ranges (T_{str} — T_{an})

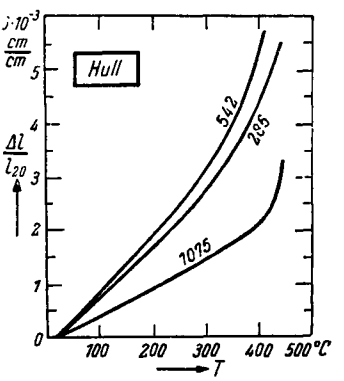
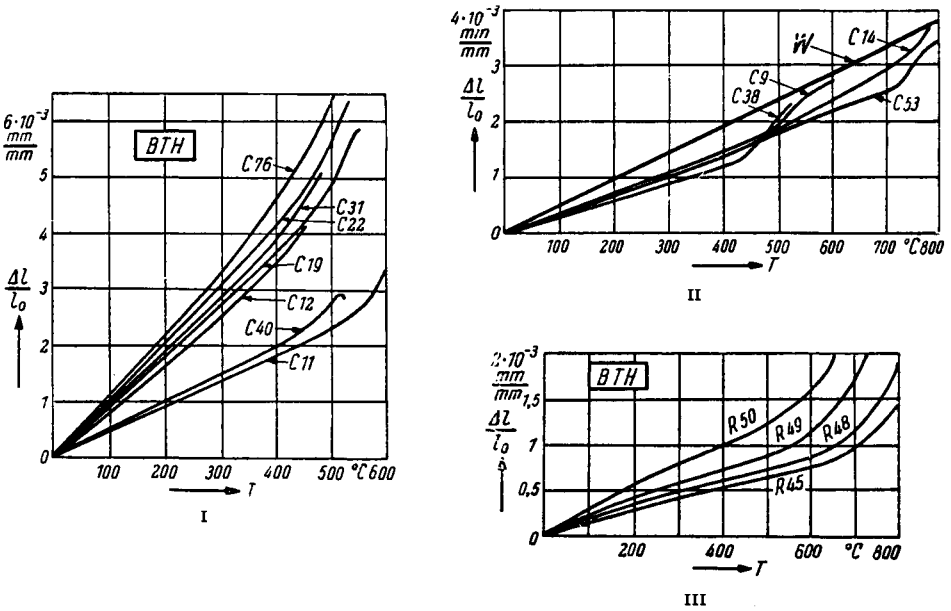


Fig. B 10-30 Expansion characteristics of a few American sealing glasses from [2]HULL (cf. also Tables T 10–2 and T10–4, A 2)



[10.2]

Fig. B 10-31 Expansion characteristics for glasses made by BRITISH THOMSON–HOUSTON (cf. Table T 10-4, E 1)

I soft glasses and Mo-sealing glasses; II tungsten-sealing glasses; III very hard glasses (intermediate) ($\alpha(0\text{–}400) = 13\text{–}25 \times 10^{-7}$ /°C)

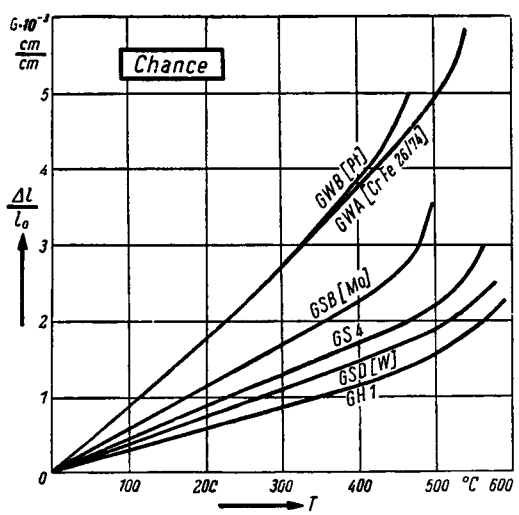


Fig. B 10-32 Expansion characteristics of some sealing glasses made by CHANCE BROS. Matching sealing metals in brackets [ ]. (Cf. also Table T 10-4, E 2.)

[10.2]

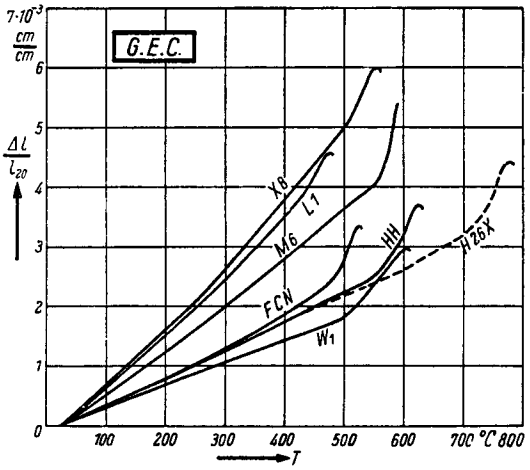


Fig. B 10-33 Expansion characteristics of glasses made by the GEN. ELEC. Co. (GEC), Wembley, England (cf. Table T 10–4, E 3)

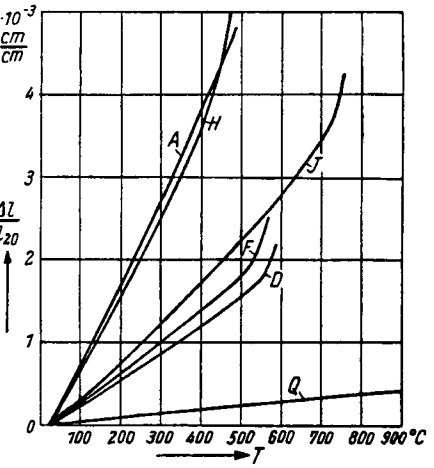


Fig. B 10-34 Expansion curves of DOUGLAS glasses (composition see Table T 10–2, E 4) (from [1]DOUGLAS)
Q quartz glass

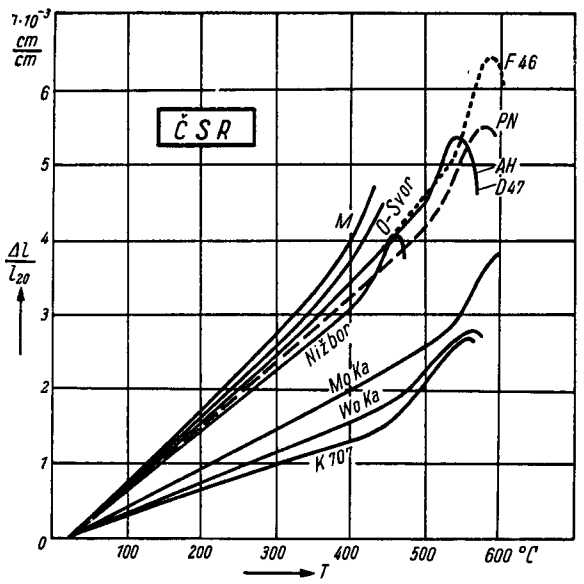
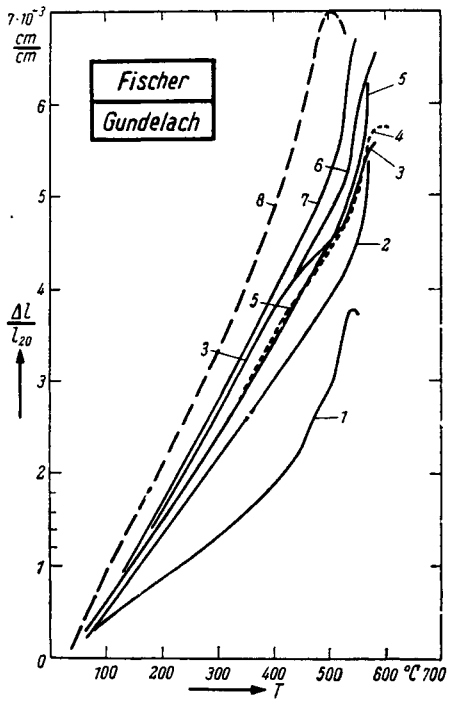


Fig. B 10-35 Expansion curves of technical glasses made in Czechoslovakia (cf. also Table T 10–4, C)

TYPE	MEAN EXPANSION COEFFICIENT (10^{-7}/°C) IN THE TEMPERATURE RANGE				
	20–100 °C	20–200 °C	20–300 °C	20–400 °C	20–500 °C
D 47	82.6	85.3	88.0	90.7	93.8
KI A	85.7	88.5	91.3	94.1	—
Kovar K 705	46.4	46.1	47.7	77.2	—
K 707 low-loss glass	33.4	33.5	33.7	33.9	—
Molybdenum MoKa	47.3	48.4	50.3	52.1	53.8
PN	76.8	79.3	81.8	84.3	86.8
Tungsten WoKa	38.2	39.5	40.5	41.5	—

[10.2]



FISCHER GLASSES	CURVE NO.
Ampullax	5
Fe-sealing	8
GeGeF	4
M glass	2
Mo glass	1
Prima glass	6
Pt glass	3 (1)

GUNDELACH GLASS	CURVE NO.
Apparatus glass	7

Fig. B 10-36 Expansion characteristics of some FISCHER glasses and one GUNDELACH glass (measurements taken at SIEMENSRÖHRENWERK)(1) (cf. also Table T 10–4, D3 and D6)

(1) The glass of curve 3 was obviously poorly annealed.

[10.2]

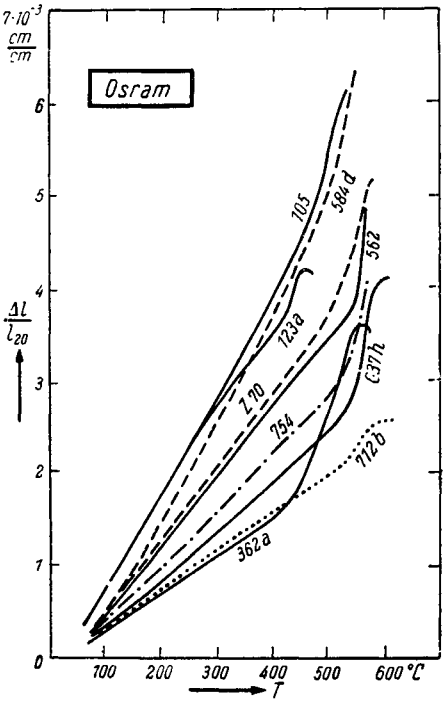


Fig. B 10-37 Expansion curves of OSRAM K.G. glasses (cf. Table T 10–4, D 8)

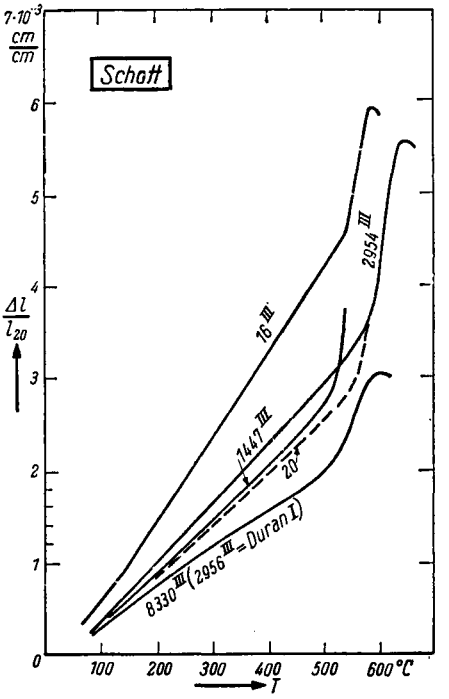


Fig. B 10-38 Expansion curves of some SCHOTT glasses (from measurements made at the SIEMENSRÖHRENWERK); cf. also Table T 10–4, D 9 and D 22

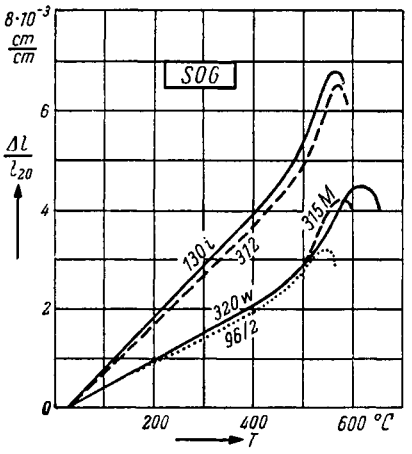


Fig. B 10-39 Expansion curves of two sealing glasses of the SENDLINGER OPTISCHE GLASWERKE (SOG) (from [6]ESPE) (cf. also Table T 10–4, D 11)

10.2.V. *Thermal Shock Resistance*[27] *of Technical Glasses*

The expansion coefficient is of great interest in yet another respect for the working and use of glass. Essentially, it determines the resistance of a glass, within the brittle range, to sudden temperature variations without rupture; that is, to thermal shocks, which are very frequent in vacuum work.[28] Sudden cooling is particularly hazardous; the hot glass at the first contact point with the cold medium is cooled there more rapidly than at some distant point, and this sets up local shrinkage, and hence momentary [10.2]

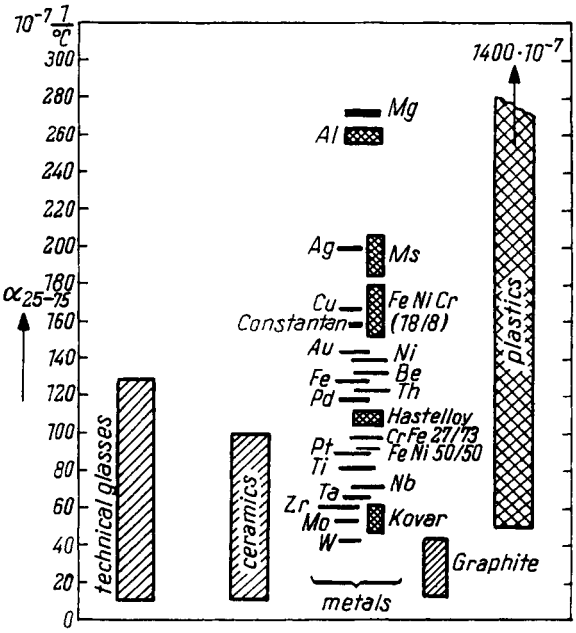


Fig. B 10-40 Range of expansion coefficients α (25–75) (1/°C) of technical glasses, compared with other materials

tensile stresses, especially at the surface. Glass has low tensile strength and therefore is not easily able to support these stresses, particularly as there are always areas on the surface where resistance is reduced (scratches) which lead to cracks and thence to failure (notch effect). The dangerous tensile stresses are higher the more intensive the shrinkage, i.e. the larger the impressed temperature gradient, and the higher the expansion coefficient. (An extreme case of this is pure quartz glass; its abnormally low α allows red-hot material to be plunged into *cold* water without fracture occurring.) Conversely, rapid heating leads to superficial compressive stress which is less dangerous because glass has good compressive strength.

[27] "Temperaturwechselbeständigkeit" is now the official German term, stipulated in DIN 52325. Other terms are also found in the older literature (see German text of this book, p. 99). The most frequent expression in Anglo-American publications is "thermal shock resistance".

[28] E.g.: sudden switch-on of a W lamp-filament or cathode near a glass wall, cooling by rain of the hot envelope of a running lamp, relatively rapid cooling of formed glass parts below the transformation range after annealing, and similar processes.

Naturally, thermal shock resistance is influenced by other properties than α. According to the SCHOTT–WINKELMANN equation (see ZSCHIMMER), in the case of sudden cooling thermal shock resistance expressed as the just-tolerable temperature difference ΔT is related to other parameters by

$$\Delta T = \frac{\sigma_{zB}}{E\,\alpha}\sqrt{\frac{\lambda}{\gamma c}}\,W,$$

where σ_{zB} is tensile strength, E the elastic modulus, α the thermal expansion coefficient, [10.2] λ thermal conductivity, γ the density and c the specific heat. W is a shape factor, a number which depends only on the dimensions and geometry of the piece. Since all the parameters in the equation except α vary only relatively little from one type of glass to another, the expansion coefficient is the predominant influence on thermal shock resistance.

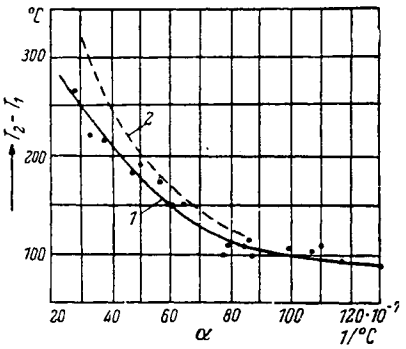


Fig. B 10-41 Thermal shock resistance $\Delta T = T_2 - T_1$ of glass test samples of equal size and same shape, as indicated by the sudden cooling (from T_2 to T_1) that they can just withstand without fracture; plotted as a function of thermal expansion coefficient α of the types of glass concerned (T_1 usually = 20 °C approx.)
1 measured on 5 mm thick, 30 mm long rod, end rounded off (SCHÖNBORN), *2* measured on beakers (GOULD)

Measurements made on geometrically similar test samples have proved the validity of the SCHOTT–WINKELMANN equation for all technical glasses of fairly normal composition, and hence the overriding influence of α (see Fig. B 10-41). Only glasses of abnormally high alumina, baria, or lead content show a somewhat lower thermal shock resistance than that which corresponds with their α values.

Since in general hard glasses have lower α s, they are also "hard" in the sense of higher thermal shock resistance. It should be remembered, however, that there are glasses of low α which soften at the same temperature as soft glasses; e.g. so-called Kovar glasses, with α about 50×10^{-7}(1/°C) and T_g about 420°. Such glasses are only hard in the sense that they have high thermal shock resistance, but are soft according to their transition temperature point or annealing range.

Obviously, whatever method is used for measuring thermal shock resistance, only a relative figure is obtained, and therefore only a sequence of *types* of glass. The actual thermal shock resistance of a particular glass body depends on the type of glass, but also very much on the way it was annealed or heated, and as already stated, on the dimensions of the test-piece, especially the thickness. A thin piece is less sensitive to sudden change of temperature than a thick one.[29] This is also the reason why individual

[29] According to [4]VOLF, the rule of thumb which holds for cylindrical glass vessels (beakers) below 1 mm thickness of wall is:

Thermal shock resistance $= T_2 - T_1 = 10{,}000/\alpha \times 10^7$ (°C),

for example $\alpha = 50 \times 10^{-7}$ (1/°C); the thermal shock resistance = 10,000/50 = 200°. For thicker walls of d (mm) we have

Thermal shock resistance $= (1/\sqrt{d}) \cdot 10{,}000/\alpha \times 10^7$ (°C).

For example, if d for a beaker of the same type of glass is 4 mm, thermal shock resistance = only 100°.

measurements of thermal shock resistance differ by 40–50°, so that a large number of determinations must be made on pieces of equal dimensions if a really reliable average is to be found. It is clear that thermal shock resistance values will depend strongly on the presence of stresses, and hence on the state of anneal of the test-piece, and also on its surface condition (scratches, cracks).

Methods of measurements of thermal shock resistance. The details are more or less arbitrary and are only fixed by the effort to reduce uncertainty due to the shape factor to a minimum.

According to the latest DIN 52325 (1953), the test-pieces are rods of 30 ± 0.2 mm length and dia. $= 6 \pm 0.2$ mm; the cut edges should be lightly rounded off by melting, and the piece then carefully annealed. Ten of them are heated to the first quenching temperature of 80° in a tilting furnace and held there for 10 minutes. They are then dropped 100 mm into a beaker containing 1 liter of water at 20°, on whose bottom lies a fitting wire sieve which can be withdrawn. When the samples have been withdrawn, the cracked ones are separated from the rest, which are then tested again at 10° higher, and so on until all exhibit cracks. After another ten samples have been given the same test, the quenching temperatures at which the individual samples cracked are averaged for all twenty samples. The thermal shock resistance is obtained from this value by subtracting the cold-water temperatures.[30] Values found by this method are given in Table T 10–4, D 8 (OSRAM) and D 9 (SCHOTT). [10.2]

The test used in Czechoslovakia is similar.[31]

CORNING GLASS WORKS measure thermal shock resistance on annealed but not tempered glass plates 150×150 mm² (6×6 in.²), thicknesses $^1/_8$, $^1/_4$ and $^1/_2$ in. Some values are given in Table T 10–4, A 1. For soft glasses, thermal shock resistance values on 6 mm thick plates are about 50°, and for hard glasses about 150°; for high-silicate glasses (95% SiO_2) it can be as high as 1000° (cf. also Table T 10–3). If glasses are subjected to prolonged tempering, their thermal shock resistance can rise to twice those of glasses annealed in the ordinary way.

The American way ([2]ASTM) of testing glassware, bulbs, beakers, etc., is to immerse them alternately in hot and cold water by automatic devices. The German standard is still in the development stage. Czechoslovakian practice ([1]ANON.) is to *heat* a piece of hollow-ware; it is quickly filled with hot water (100°) or hot oil (above 100°) when it is at room temperature (*ca.* 20°) and in fact liter-capacity samples can be filled at 1 liter/

[30] Example: of 20 samples which cracked on quenching, the number which cracked at given temperatures were:

2 at 160°;	2 × 160 = 320	Average quench temp. 3760/20	= 188°
1 at 170°;	1 × 170 = 170	Measured average water temp.	= 20.5°
5 at 180°;	5 × 180 = 900	hence thermal shock resistance to nearest 1 °C	= 168
7 at 190°;	7 × 190 = 1330		
3 at 200°;	3 × 200 = 600		
0 at 210°;	0		
2 at 220°;	2 × 220 = 440		
20	3760		

[31] Total of 50 rods of 30 ± 1 mm length of glass of average thermal shock resistance values, and of 80 ± 1 mm length of higher thermal shock resistance, dia. $= 5 \pm 0.2$ mm, groups of 5 tested, heating by 5° steps until all are cracked. Thermal shock resistance calculated by DIN 52325.

sec, up to 5 liters at 2 liters/sec, 20 liters at 3 liters/sec and over 50 liters at 5 liters/sec. Testing is started at 90° and the temperature of the filling fluid raised in 10° steps until the sample cracks. The thermal shock resistance is then the difference in temperature before and after filling with hot fluid. This is usually higher than the thermal shock resistance found by external cooling. The latter test involves filling the sample with a hot fluid, stirring continuously, immersing the sample in water at 20°, and determining the temperature difference and cracking point and the time that elapses before cracking after immersion.

[10.2]

10.2.VI. *(Static) Thermal Stress Resistance*

In addition to the resistance that glass shows to rapid changes in thermal stress, another property is of technical interest: its ability when in the brittle state to withstand, without rupture, temporally constant but spatially variant temperatures (thermal drops) of the kind that occur in practice due to one-sided thermal stresses.[32] These spatial variations of temperature naturally produce spatial or local variations in expansion which lead to stresses which are compressive on the hotter side and tensile on the cooler. Their magnitude is given by:

$$S = \alpha \cdot E \cdot \Delta T/2(1 - \mu),$$

where ΔT is the thermal gradient (°C) between the surfaces, E is Young's modulus (kg/mm²), α the expansion coefficient of the glass (1/°C), and μ is Poisson's ratio. To evaluate the temperature drops that a glass body can reliably withstand, CORNING Works find, for their commercial glass, that difference in T which will produce at the cooler surface of a tube or disk a tensile stress of 1000 psi (= 0.7 kg/mm²) and which can therefore be withstood by glass with a safety factor of about 10 (σ_{zB} = 5–8 kg/mm²). The above equation yields for static thermal stress resistance if μ is put equal to *ca.* 0.23,

$$\text{thermal stress resistance} = 1.4\,(1 - \mu) \cdot (1/\alpha)/E = 1.08/E \cdot \alpha\ (°C).^{33}$$

The values given by CORNING for thermal stress resistance are found in Table T 10–4, A1. For glass of pronounced softness, they amount to about 20°, and for very hard glasses about 200° or less (see also Table T 10–3).

10.2.VII. *Thermal After-effects on Expansion*

(see also GRUNDMANN, THIENE)

If a glass is heated to high temperature and then slowly cooled, it shows no stresses, but one can observe that the expansion caused by the heating process does not disappear at once or completely, but a residual amount remains that is only gradually lost. Usually,

[32] Examples: (a) glass window in a tube or vacuum furnace, strongly heated from inside by radiation, from outside cooled by forced draught; (b) pinch-foot with one or more current leads (glass-metal seals) strongly heated by passage of current.

[33] Example from Table T 10–4, A1, for CORNING 7740 (Pyrex type) with E = 6900 kg/mm², and α = 32 × 10⁻⁷ 1/°C:

$$\text{thermal stress resistance} = 1.08/6900 \times 32 \times 10^{-7} \approx 49°$$

(= 48° from CORNING data). Therefore, a glass window of a furnace whose inner surface is heated to 148° by radiation from the furnace and whose outer surface has assumed the temperature of 100° by natural convection or artificial cooling, will experience a tensile stress of 0.7 kg/mm². For the case of forced cooling, it should be pointed out that the outer surface temperature cannot be set equal to that of the coolant (e.g. the cool air-stream flowing past) in such calculations.

this thermal after effect (so-called) causes no trouble in vacuum work, and only in the manufacture of thermometers is it inconvenient; newly made thermometers exhibit ice-point (zero) drift, because of the gradual contraction of the glass capillary, in the direction of higher calibration values. Since this instability takes years to decay, it is known as the "secular rise of the ice-point". By "artificial aging", which means prolonged heating and slow cooling of the capillary (see, e.g., Table T 10–7, col. 7), this zero drift can be reduced to harmless amounts. For satisfactory aging of thermometer glasses, a good recipe ([2]EBERT) is to heat the glass for about 3 hr at 20–30° above the T_g, cool to T_g in 3 hours, and hold it there for 6 hours.

However, even with aged and then calibrated thermometers of the usual glass, this thermal after-effect occurs in that directly after the thermometer has been heated in use, a residual expansion of the capillary remains, manifesting itself in a lowering of the ice-point reading relative to the scale zero. This is called the "ice-point depression". If a properly aged thermometer is heated to 100° and then cooled to 0°, the shift in zero point in °C is the "depression constant" for the type of glass involved. Thermometers made of the usual Thüringer apparatus glass have a constant of *ca.* 0.4° so that the null point and with it the whole visible scale is *ca.* 0.4° out after every measurement made around the 100° mark. After a few days this error disappears and the thermometer reads correctly again.

Successful attempts have been made to develop special thermometer glasses with very low depression constants, and this became possible once it had been discovered that the constant mainly depended on the alkali content; glasses which contain potassium and sodium oxides have larger thermal after-effects than those which contain only one or the other. These special glasses, such as No. 16^{III} in Table T 10-2, D 9, have so small a depression

TABLE T 10–7. DEPRESSION CONSTANTS AND A FEW OTHER IMPORTANT DATA OF JENA THERMOMETER GLASSES (MANUFAKTURER: SCHOTT UND GEN.)

DESIGNATION	HYDROL. CLASSIFICATION	α (10^{-7}/°C)	LIMITS IN USE (°C)	T_g (°C)	DEPRESSION CONSTANT (°C)	AGING TREATMENT[1]			
						hold	cool	hold	cool
16^{III}[2]	II	80	360 (460)	530	0.04	3 h 545 °C	3 h → 480 °C	6 h 480 °C	Slowly to room temperature
59^{III}	I	57	510	560	0.03	3 h 555 °C	3 h → 500 °C	6 h 500 °C	
2950^{III} / (3058^{III}) Supremax	I	33	625	730	0.03	3 h 700 °C	3 h → 640 °C	6 h 640 °C	
2954^{III}[3]		60	525	573	0.015				
For comparison: NW glass[4]	III	79	460	540	0.04				
Thüringer apparatus glass		≈90	≈460	≈450	≈0.41				

(1) From [1]VOLF. (2) Red-violet stripes, same as PN glass Polubný–CSSR, see also Table T 10–4, C. (3) Black stripes.
(4) Mfr.: GLASWERK WERTHEIM. Coded with 2 yellow stripes.

[10.2]

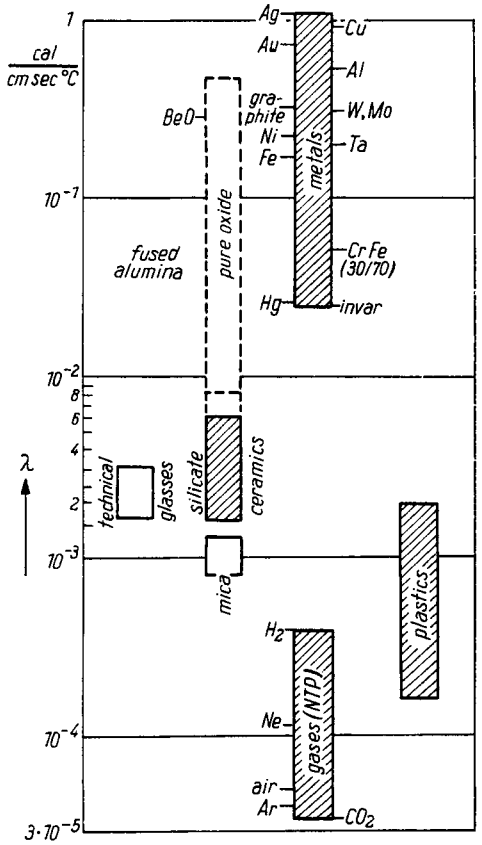


Fig. B 10-42 Comparison of the thermal conductivities λ at 20 °C of technical glasses with other materials

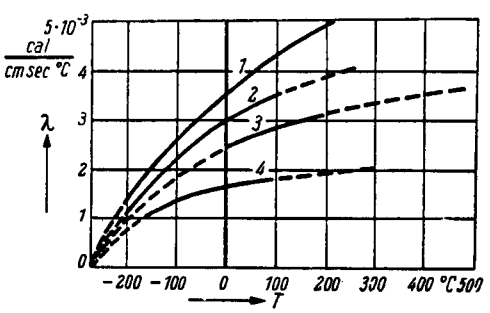


Fig. B 10-43 Thermal conductivity λ of technical glasses as functions of temperature T

1 quartz glass (see, however, Fig. B 11-5c), *2* borosilicate glass, *3* soda-lime glasses (average), *4* heavy lead-glass, 40–50% PbO

constant that it can be virtually neglected in making thermometers (see Table T 10–7). Pure quartz glass shows almost no thermal after-effect and is therefore the ideal material for precision thermometers without depression phenomena.

10.2.VIII. *Thermal Conductivity of Technical Glasses*

([1]GEHLHOFF, RUSS)

The value is important when there are thermal gradients in the glass, e.g. in thermal conduction from hot-running metal-to-glass seals to glass. As the comparison diagram Fig. B 10-42 shows, λ is very low compared to that for metals. Because of this, very poor thermal equalization occurs during uneven heating or cooling of a work-piece, and very large differences in thermal expansion build up even between areas that are close; continuous or transient mechanical strains are set up, depending on whether the uneven thermal processes take place when the glass is in the annealing range (thus at least partly above T_g) or in the brittle state (thus definitely below T_g).

There is relatively little difference between the λ s of individual types of glass. The highest is that of pure quartz (at 20° *ca.* 3.3×10^{-3} cal/cm sec °C). The addition of glass-forming oxides lowers λ according to the type and amount. Of the technical glasses, the highest is that of borates, up to 3×10^{-3}. Magnesia, alumina and iron oxide glasses are fairly good conductors, and zinc or lime glasses are less so. The lowest λ s are those of baryta and lead glasses, as low as 1.6×10^{-3}. λ increases somewhat with rising temperature (see Fig. B 10-43).

Although there are cases in glass vacuum tubes where the heat is mostly conducted away by the glass wall,[34] it is better to use metals for tube walls whose heat is removed by external means, water-cooling, forced draught, or fins. Most of the thermal energy produced electrically in a glass vacuum tube is removed by radiation through the wall, since the majority of technical glasses are highly transparent to thermal radiation (see Section 10.2.XVI).

However, the low λ of glass is very desirable in metal-vapor-filled discharge tubes where, in order to have a sufficiently high vapor pressure, a high temperature has to be produced over the whole discharge space, and thermal conduction along or through the wall must be prevented so far as possible.[35] [10.2]

10.2.IX. *Specific Heat of Technical Glasses*

Values lie between 0.08 and 0.23 cal/g °C; this is an average measured in the range 0–100°. Pyrex (Tables T 10–2, A1, and T 10–4, A1) has a value of 0.2 (17–100°), Sial glass has 0.1975 (Tables T 10–2, C, and 10–4, C). The specific heat generally rises with temperature (see, e.g., Fig. B 10-43A).

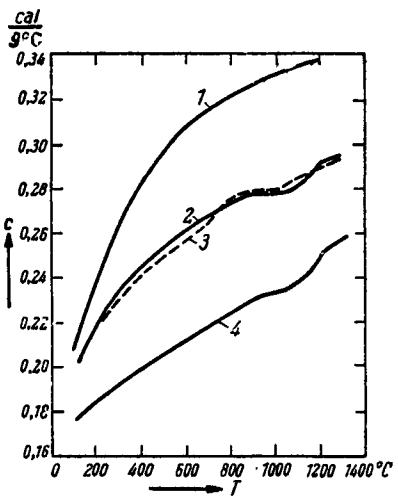


Fig. B 10-43A Specific heat c of 3 soda-lime glasses (1–3) and 1 potash lead silicate glass with 19% PbO (4) as functions of temperature T. ([1]GEHLHOFF, HARTMANN)

10.2.X. *Electrical Conductivity x and Volume Resistivity ϱ of Technical Glasses*

At low temperatures and not too high voltages, the ordinary glasses are very good insulators. Their ϱ values are relatively high compared with other insulators, and at room temperature lie between 10^{11} and 10^{19} Ω-cm, depending on the type of glass. (By volume resistivity is meant the resistance of the mass of the body, exclusive of any surface leakage, which is mostly the result of conducting layers of contaminant such as an adsorbed water film.) Values are given in Fig. B 10-44. Glass is a conductor of the second class: current carriers at low temperatures (below 430°) are almost exclusively Na^+ ions, and to a lesser degree K^+ ions. At elevated temperatures, the modifier ions like Ca^{++} and Ba^{++} contribute to the conductivity.

At constant temperature, Ohm's law holds for low fields, and for higher field strengths (E) the conductivity obeys the equation

$$x = x_0 \, e^{a+bE},$$

where a, b, and x_0 are constants. ϱ falls as temperature rises because of the increasing

[34] Examples: (a) glass wall of the dome of an air-cooled Hg rectifier; (b) glass wall of a small-diameter discharge tube, such as a luminous tube, where considerable heat is developed at the wall itself by extensive carrier recombination.

[35] An example is the well-known sodium lamp in which a temperature of 270° must obtain over the whole vacuum space so as to produce a Na vapor pressure of 10^{-2} Torr to achieve intense illumination (see 20.6.V).

mobility of the charge carriers, usually according to the RASCH–HINRICHSEN equation

$$\varrho = Ce^{B/T} \quad \text{or} \quad \log \varrho = A + B/T;$$

many types follow the law

$$\varrho = C' e^{-B'T} \quad \text{or} \quad \log \varrho = A' - B' \cdot T,$$

according to [1]STEVELS, where A, A', B, B', C, C' are constants and T (°K) is the absolute temperature. In the latter case, plotting ϱ on logarithmic scale against T, and in the former case against $1/T$, will give a straight line.[36]

[10.2]

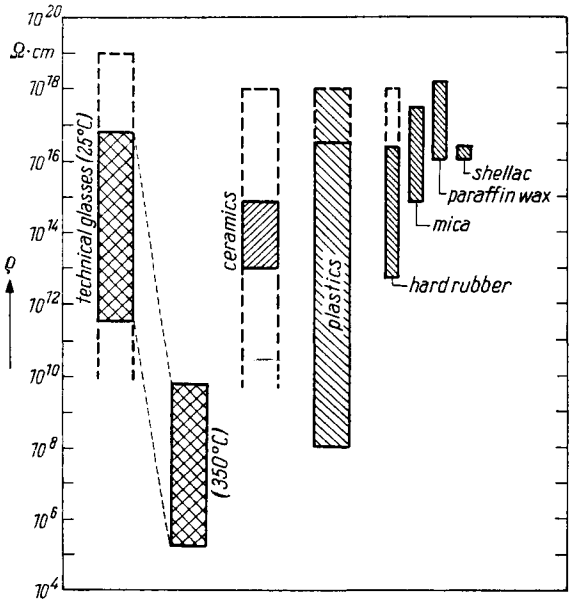


Fig. B 10–44 Volume resistivity ϱ of technical glasses at room temperature in comparison with other insulators

The resistance lines $\log \varrho = f(1/T)$ show a fairly sharp knee at the transition temperature which can be used to fix this important parameter, as already stated. Above this point, the functions remain linear even though the slope may be different, only becoming curved at very high temperatures; the specific resistance can fall to 1–10 Ω-cm at 1200 to 1400°. Figure B 10-45 gives the resistance functions for a series of typical glasses. As can be seen, these "resistance lines" have almost the same slopes and simply occupy different temperature regions, i.e. the constant B is not too different for the various types of glass between room and transition temperature.[37] In Europe it is generally regarded

[36] The divergent behavior of the two glass groups is only really noticeable at low temperatures, since those of the STEVELS group are more or less independent of T from 200° up, which is not the case for the other group. This raises the question whether the RASCH group may also exhibit this behavior but at temperatures below room temperature (ETZRODT).

[37] In Fig. B 10-53, taken with the same apparatus, the constants B of 20 different glasses lie in a range of only 5×10^3 to 6×10^3; A lies between −4.2 (poor glass) and +1.3 (EM glass). According to measurements on 178 types of Jena optical glass, B varied in most cases between 4.5×10^3 and 8×10^3, while A lay between −3 and +1.5 (BEYERSDORFER).

as a sufficiently good index of the insulating property of a glass just to give a few temperatures at which the conductivity resistance has certain definite values. For practical reasons a standard value is $100 \times 10^{-10}\ \Omega^{-1}\text{-cm}^{-1}$ (corresponding to resistance 100 MΩ-cm)[38] and is called the $T_{\varkappa 100}$ point ([1,5]GEHLHOFF) or recently also the $T_{\varrho 100}$ point. This, [10.2]

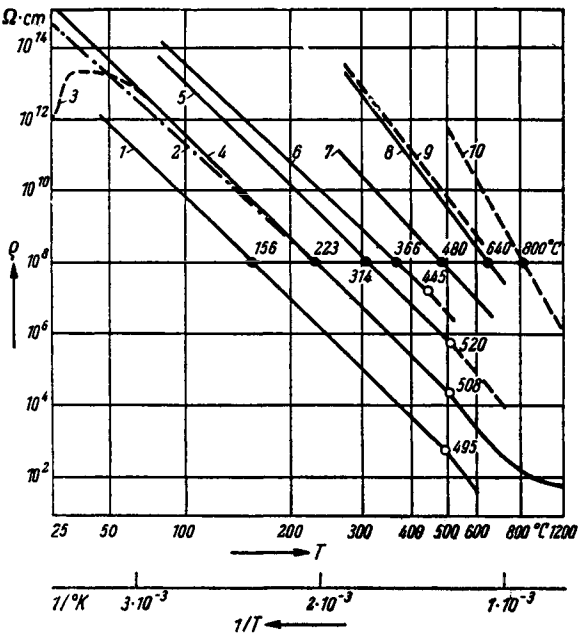


Fig. B 10-45 Resistance characteristics of typical glasses: resistivity plotted on log scale as a function of reciprocal absolute temperature ($1/T$)

Thüringer glass curves (3 and 4 from [1]GEHLHOFF) and curves 8–10 are experimentally determined; those of the other glasses are based on the $T_{\varkappa 100}$ point for 10^8 Ω-cm

● $T_{\varkappa 100}$ points

○ transformation points (knee of the curve)

TYPE OF GLASS	CURVE NUMBER	TYPE OF GLASS	CURVE NUMBER
Alumoborosilicate, alkali-free	9	Thüringer glass, alumolime silicate, with H_2O layer	3
Lime magnesia glass	1	As 3, but no H_2O skin	4
Osira 14, hard glass	7	W-glass (Pb-borosilicate)	5
Osira 15, hard glass	8	For comparison: quartz single crystal, v. pure	10
Pt-sealing glass (Pb-silicate)	6		
Pyrex glass (borosilicate)	2		

therefore, gives a guide to how much more or less a given glass may be heated than another to obtain the same conductivity, other things being equal, but for precise plotting of the resistance lines it is better not to trust to the parallelism mentioned; one should specify two ϱ values at two different temperatures (say 250 and 350°) with the

[38] It is inconvenient to measure higher resistance values; at low values there is the danger of exceeding the transition temperature and the temperature value so obtained cannot be used to construct the resistance lines (cf. Fig. B 10-45).

[10.2]

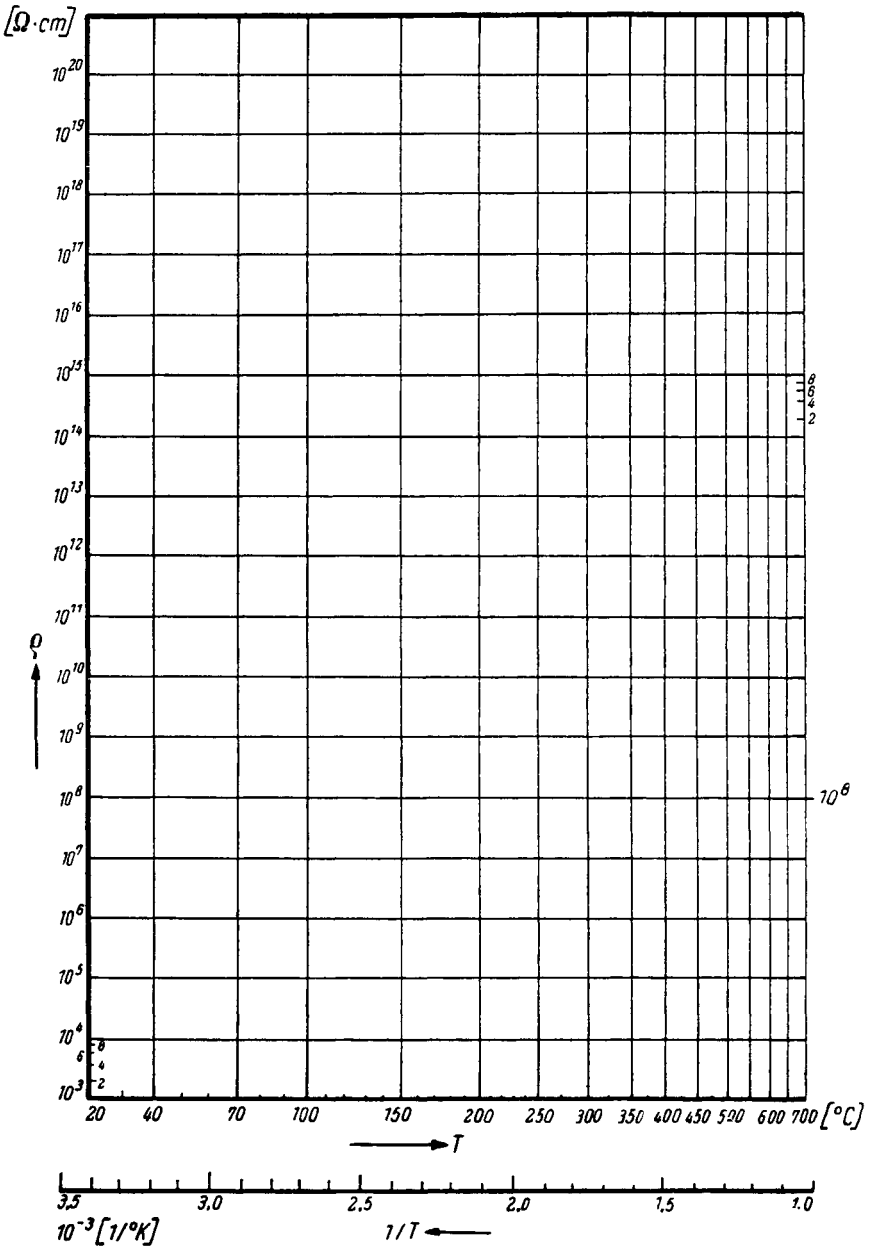


Fig. B 10-46 Coordinate paper, $\log \varrho = f(1/T)$, for plotting the "resistance lines" of technical glasses

help of which it is possible to draw each line precisely without the aid of other lines, and to obtain accurate extrapolated ϱ values (>100°) at temperatures far from the $T_{\varkappa 100}$ point. To facilitate the plotting of these resistance lines and extrapolations, a coordinate diagram $\log\varrho = f(1/T)$ is given for the range of interest, in which ϱ (Ω-cm) and T (°C) scales are provided. However, in such extrapolations it is necessary to be cautious with values below 100°, since here surface layers exist and also, apparently, deviations from the RASCH–HINRICHSEN equation which reduce the ϱ values obtained. Obviously the same must apply above the transition temperature, but results in this range are mostly without interest for applications in lamp and tube glasses. [10.2]

Strained and unstabilized glass has a lower resistivity than well-stabilized material. Figure B 10-47 is instructive on this point; it shows (*a*) a $\log\varrho = f(1/T)$ curve for rapid

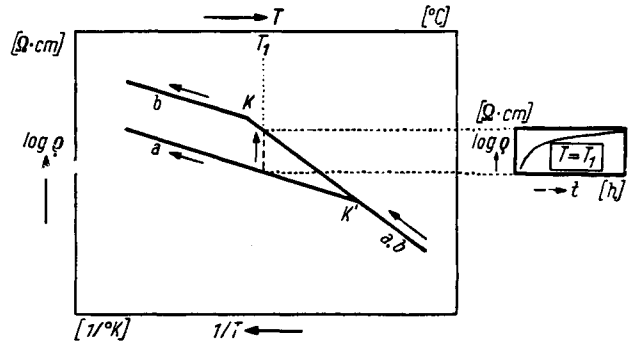


Fig. B 10-47 The resistance line $\log\varrho = f(1/T)$, across the annealing region T_{an} to T_{str}; *a* with rapid cooling, *b* with slow cooling of the test sample ([1]KIRBY)

If the rapidly cooled sample is held at T_1 for a long period t, as stabilization increases, the resistance ϱ rises from the curve *a* value to that of *b* at the same temperature (cf. also Fig. B 10-56A)

cooling and (*b*) for slow cooling while traversing the stress-relieving range (cf. also Fig. B 10-56A). If one keeps a rapidly cooled (unstable) glass for a long time at constant temperature in the annealing range, stabilization proceeds and as time goes on the original, low ϱ of the rapidly cooled glass rises to the higher value of slowly cooled, stabilized glass (see right-hand diagram in Fig. B 10-47). At the same time one can see that taking the resistance line only gives the right transition temperature as the knee K if the annealing range is traversed slowly and if the glass is strain-free; otherwise too high a value is obtained (K').

Measurement of the electrical resistance of glasses. This is carried out in a furnace if temperature dependence is required. The simplest way is to use two metal wires or strips sealed into the glass, and having the same expansion coefficients, i.e. Pt electrodes for glasses with expansions of 90×10^{-7}, and Mo wire for those of 50×10^{-7}/°C. In the latter case it is recommended that the measurements are carried out in a N_2 atmosphere to prevent oxidation of the wire. Figure B 10-48 shows a precision method. As shown, two test rods are used (P_1 and P_2); tubes, parallel-ground flat disks, or square glass plates can also be employed. The ends are ground and platinized. A Pt contact shim is inserted between them and they are clamped between two Pt contacts in a screw vise

of Al and Cu to compensate for expansion. The measuring voltage is applied between the central contact K and the two end contacts K_1, K_2, which are connected to each other; this provides excellent isolation of the test-pieces in a simple way. A device built on essentially the same principle is shown in Fig. B 10-48A; here, the compensation for the clamp expansion is provided by a spring outside the furnace.

The heating or cooling rate should not exceed 0.5°/min when measuring the $\varrho - T$ characteristic of glasses. Between 10^4 and 10^{10} Ω-cm, a galvanometer can be used to

[10.2]

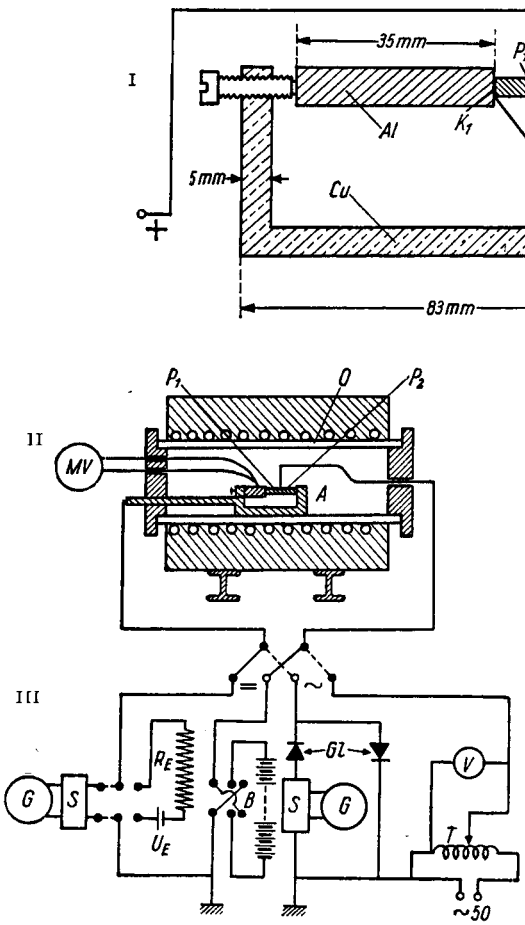


Fig. B 10-48 Apparatus for measuring the resistivity of glasses at elevated temperatures in the brittle and annealing ranges (MEUNIER)

I, support screw-clamp (made of Cu and Al to compensate for thermal expansion) holding two test-rods P_1 and P_2 (each 8 mm long, 4 mm dia., with silvered ends), K central Pt contact, K_1 and K_2 side contacts; II, furnace O with screw-clamp A, test-samples P, thermel and millivolt meter; III, circuit diagram for D.C. and A.C., G galvanometer with shunt S, B D.C. supply, 90 V battery, U_E and R_E galvanometer calibration circuit, Gl metal rectifier plates, T Variac-type transformer, V A.C. voltmeter

measure the potential drop; with higher resistances, measurements are made of loss of charge of a shunt capacitor in a fixed time, using a ballistic galvanometer to avoid electrolysis and polarization phenomena, D.C. measuring voltages are only applied for short times (about 5 minutes) and from time to time polarity should be reversed. A.C. can also be applied (see Fig. B 10-48) or low-frequency square waves, say 18 c/s (BEYERSDORFER, [2]KIRBY), or one can work with an audio-frequency bridge. A large

initial current is often observed at switch-on which does not disappear until above 100°, and is attributable to conducting layers of moisture (see Fig. B 10-45, curve 3 for Thüringer glass at low temperatures).

This type of apparatus will measure the conductance of glass up to deformation temperature M_g, and so the characteristic knee can be found which indicates the transition temperature T_g. See, e.g., BABCOCK, HALLA for an experimental set-up to measure the conductance of glass *melts* between 500 and 1400°.

Results. Figures B 10-49 to B 10-53 give the results of measurements of resistivity of glasses, obtained in practice. As can be seen, conductance depends very strongly on the [10.2]

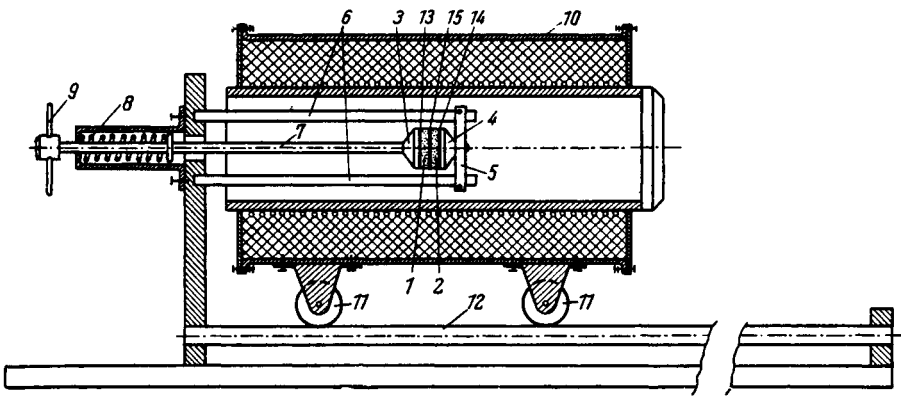


Fig. B 10-48A Apparatus for measuring the electrical resistivity of glasses (2ONDRÁČEK)

1, 2 glass test-pieces (disks ground plane-parallel, 5–6 mm thick, dia. 20 mm) silvered (or better, platinized) at the contact ends, and clamped between two contact plates of Ni; *3, 4* pressure plates to clamp the test-piece; *5* metal holder, attached to Calit rods *6*; *7* compression rod; *8* compression spring; *9* handgrip to release the spring; *10* furnace (up to 660°) which travels on rollers *11* and rails *12*; *13, 14, 15* contact plates of Ni (or better, Pt) with welded leads for the measuring current

composition; the $T_{\varkappa 100}$ point lies in the range 150–550°. The strongest influence on this parameter is the alkali content (see Figs. B 10-54 and B 10-54A); in particular, increasing Na_2O much reduces ϱ and with it the $T_{\varkappa 100}$ point, while the effect of K_2O is less marked. Table T 10–8, 1–4, shows that the alkali content must be kept as low as possible if high values are to be achieved. This creates difficulties however, since the viscosity and hence the working and annealing temperatures, become inconveniently high. These undesired consequences of lowering the alkali content can be offset by adding PbO, and in lesser amounts also BaO and B_2O_3. The relatively high resistivity of lead glass is due (5GEHLHOFF) only partly therefore to direct improvements in insulation from the PbO, which reduces Na^+ ion mobility by filling vacancies in the lattice with Pb^{++} ions (see Fig. B 10-55): it is more a matter of the reduction in alkali content. However, as shown by comparison of ϱ s of technical glasses (e.g. C 38 and C 12 in Table T 10–8, 2 and 5), the addition of PbO will produce the same high ϱ values in spite of high Na_2O (12%) as are obtained with low Na_2O (1.5%) and no PbO.

An unusually high ϱ is exhibited by alkali-free phosphate glasses. A special type "No. 14" (see Table T 10–2A and T 10–4A) has a value as high as $10^{12.6}$ Ω-cm at 300°,

while the corresponding value for ordinary soda-lime glass at this temperature is only about $10^{5.6}$ ([3]STANWORTH).

[10.2]

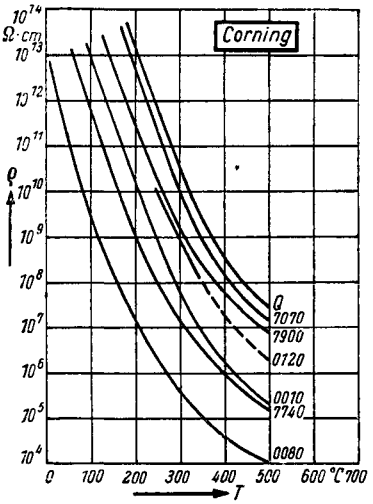


Fig. B 10-49 Electrical resistivity ϱ of CORNING glasses as functions of temperature T ([1]CORNING) (cf. also Table T 10–4, A 1); Q quartz glass

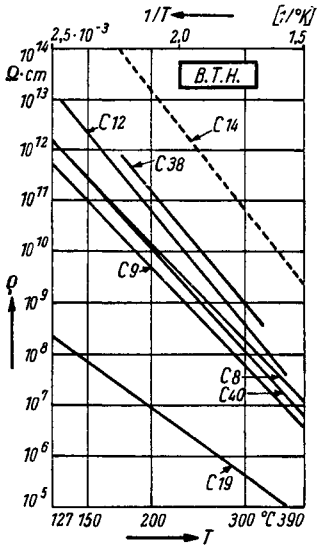


Fig. B 10-50 Electrical resistivity ϱ of glasses made by BTH as functions of temperature T (cf. also Table T 10–4, E 1)

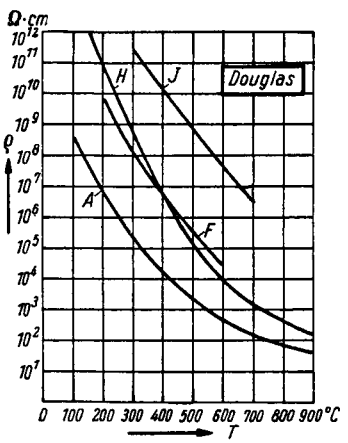


Fig. B 10-51 Electrical resistivity ϱ of glasses by DOUGLAS as functions of temperature T (DOUGLAS)

The letters refer to the compositions given in Table T 10–2, E 4

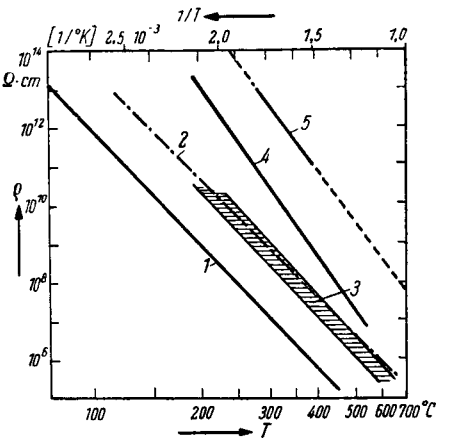
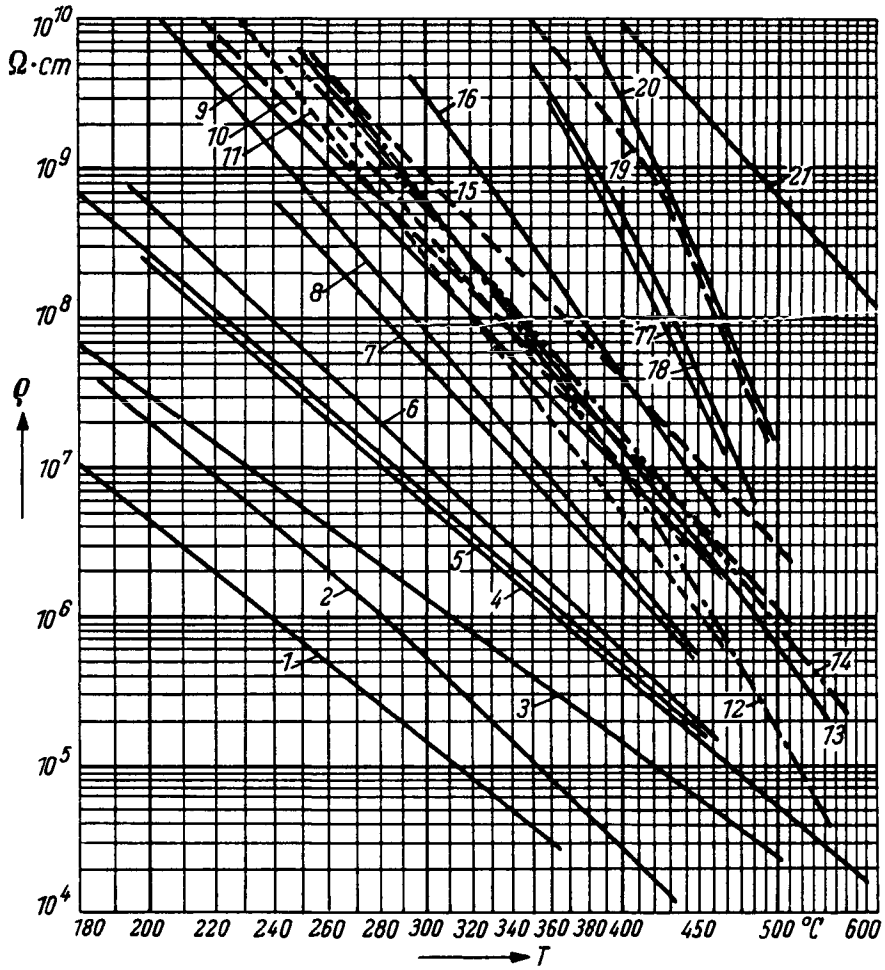


Fig. B 10-52 Electrical resistivity ϱ of various German glasses as functions of temperature T

1 FISCHER Mo-glass; *2* OSRAM glass 123; *3* OSRAM glass 362a; *4* quartz glass; *5* phosphate glass no. 14 (cf. Table T 10–4, D 3 and D 8; Tables T 10–4A and T 11–2)

It is not always possible to calculate the electrical conductivity of a glass from addition of the component values as can be done with expansion coefficients. For example,



[10.2]

Fig. B 10-53 Electrical resistivity ϱ of glasses made in France (CRISTALLERIE BACCARAT) as a function of temperature T (from MEUNIER) (see also Table T 10–4, F 1)

TRADE NAME	$T_{\times 100}$ °C	CURVE No.	TRADE NAME	$T_{\times 100}$ °C	CURVE No.	TRADE NAME	$T_{\times 100}$ °C	CURVE No.
Cristall a la sonde I	322	11	E M 264	428	17	Servitrex	≈140	1
			Neutrohm E	324	9	Strass	380	16
Cristall a la sonde II	297	8	Neutrohm P	370	15	Verre 140	345	13
			Neutrohm T	334	10	Verre 141	345	14
Cristall Q D	340	12	Omnium	≈170	2	Verre L	240	6
E M 62	467	20	Platinox	283	7	Verre Moly	223	5
E M 71	465	19	Pyrex (wartime mfr.)	220	4	A 119		
E M 263	437	18				Verre neutre	≈173	3

For comparison: quartz glass = curve No. 21

if the amount of alkali is held constant and K_2O is replaced by Na_2O, the electrical resistivity does not decrease uniformly as K is exchanged for Na. There is often an optimum (see [1]STEVELS for explanation) between all K_2O and all Na_2O content, whose position is influenced by the other components, of the glass (see Fig. B 10-56).

[10.2]

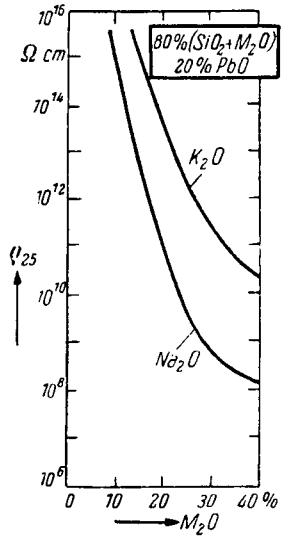


Fig. B 10-54 Resistivity at room temperature ϱ_{25} soda-lead-silicate glasses with fixed PbO content (20%) as a function of alkali content (Na_2O or K_2O) (FULDA)

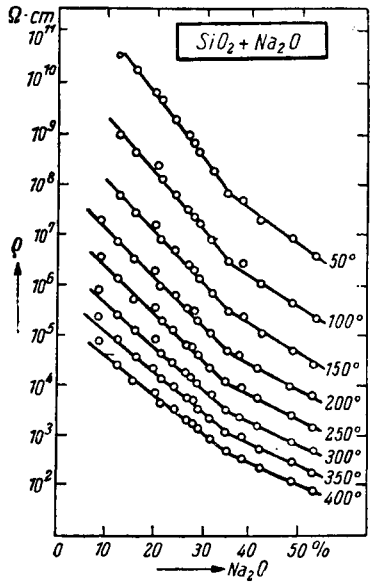


Fig. B 10-54A Resistivity ϱ_{50} to ϱ_{400} of pure sodium-silicate glasses as functions of Na_2O content (SEDDON)

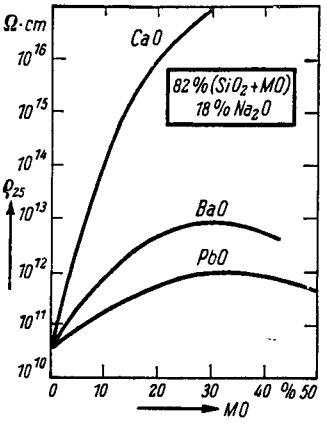


Fig. B 10-55 Electrical resistivity ϱ_{25} (at room temperature) of sodium-silicate glasses (18% Na_2O) as functions of PbO, BaO and CaO contents

In general, glasses for vacuum work are most desirable when they have high ϱ especially at elevated temperatures. However, there are cases, such as hard-glass X-ray

tubes, where a glass wall with too high a ϱ value creates the hazard of wall charges from stray electrons and hence pinholes in the wall. Special X-ray tube hard glasses have

TABLE T 10–8. EFFECT OF ALKALI AND PbO CONTENTS ON THE ELECTRICAL RESISTIVITY ϱ OF GLASS (CF. FIGS. B 10-54 AND B 10-55)

No.	TYPE OF GLASS (BTH)	α (10^{-7} 1/°C)	T_{an} (°C)	ALKALI CONTENT (%)	PbO CONTENT (%)	log ϱ (Ω-cm) at 150 °C	log ϱ (Ω-cm) at 300 °C	NOTES
1	C 14	39	720	0.8	–	(14.7)	10.9	ϱ falls with rise in alkali content
2	C 38	32	505	**1.5**	***0***[1]	**12.4**	9.2	
3	C 9	37	525	5–6	–	11.0	7.8	
4	C 19	95	530	17.3	–	8.4	5.7	
5	C 12	91	435	**12**	***30***[2]	**12.3**	8.6	Pb content raises ϱ in spite of high alkali content

[10.2]

[1] Other components of C 38: 30% B_2O_3, rest SiO_2.
[2] Other components of C 12: 1% Al_2O_3, rest SiO_2.

been specially developed for this (see Table T 10–4, A 3), which have a relatively low value of ϱ but also as high a breakdown resistance as possible. Figure B 10-56 A shows

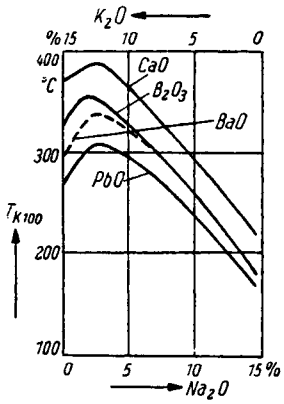


Fig. B 10-56 $T_{K\,100}$ point of ternary glasses with fixed (20%) CaO (or BaO, PbO, B_2O_3) and 15% alkali content, while only the ratio of Na_2O/K_2O is varied

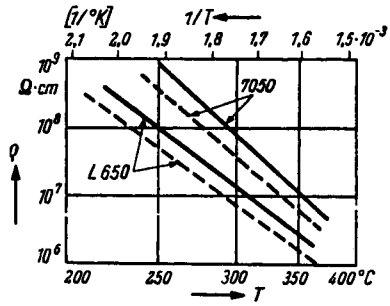


Fig. B 10-56A Electrical resistivity ϱ of a special Röntgen glass L 650 (LIBBEY-OWENS-ILLINOIS GLASS CO.), with deliberately increased electrical conductivity, as a temperature (T) function, in the strained (- - - -) and annealed (———) states

Corning glass 7050 is very similar and is shown for comparison (cf. also Table T 10–4, A 3)

the fall in ϱ of a glass of this type made by LIBBEY-OWENS, L 650, in comparison with the glass used previously, Corning 7050 hard glass. Table T 10–4, A 3, contains data on electrical rupture resistance of special X-ray tube glasses at elevated temperatures.

10.2.XI. *Electrolytic Phenomena in Glass*

([6]ESPE, [1]GALLUP, PEYSSON, RINDONE, [1]STEVELS)

The volume resistivity at room temperature of glass is high enough for most vacuum purposes. When insulation requirements are really exacting, only the surface resistivity causes any trouble (see below). However, the high temperature resistance is important when evaluating the suitability of glasses for electron tubes, especially for the pinch, since the latter may have leads sealed close together and yet up to several hundred volts apart at several hundred degrees centigrade due to radiation, thermal conductance down electrode supports and Joule heating of the seal wires. The operating temperature
[10.2] of hot-filament lamp pinch-feet of the standard type may be 150–200°. For such purposes, glasses of high $T_{\varkappa 100}$ point must be used, i.e. mainly alkali glass; the best soft glass is lead, the best hard glasses are borosilicates (cf. Fig. B 10-45).

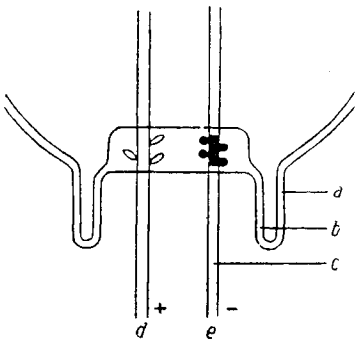


Fig. B 10-57 Schematic illustration of "lead tree" formation in a D. C.-operated hot-filament lamp

a, envelope; *b*, pinch; *c*, lead-through; *d*, cracks at the positive lead-wire; *e*, lead tree at negative lead-wire

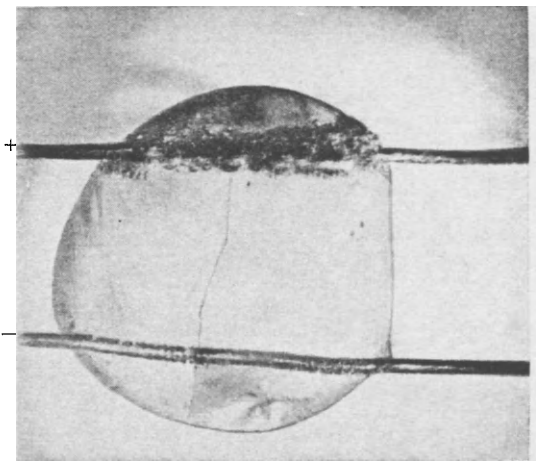
If the specific conductance or the temperature is too high, *glass electrolysis* occurs which is harmful to the life of the vacuum tube in various ways:

1. The glass between the sealed-in wires may decompose. Since alkali ions drift to the most negative electrode, which in a diode rectifier with high negative plate inverse voltage may be the anode lead, this electrode will become alkali-rich, while the most positive one will become low in alkali and develop a poorly conducting SiO_2 layer. The expansion coefficient will thus become widely different from one place to another in the same piece of glass and as time goes on, increasing strains will appear just as if glasses had been joined whose expansion coefficients were insufficiently close. The strains finally become so large that cracks form in the pinch. If the glass contains no lead, electrolytic decomposition can often be detected by brown to blue discoloration due to precipitation of colloidal alkali metals, especially near cathode leads (SCHWARZ). Discoloration and clouding near the cathode can also occur from ions of the electrode surface, which participate in this drift through the glass especially when the electrodes are of dissimilar metals. Small drop-like formations often occur at the cathode. If the foot-glass contains lead, the released alkali metal can reduce the PbO, and in the direct neighborhood of the negative lead-wire so-called "lead trees" appear, which are black, strongly branched discolorations (see Fig. B 10-57). At the positive wire of the seal, glass electrolysis releases O_2 which can lead to fine cracks (Fig. B 10-57), or the wire may be surrounded with many small O_2 bubbles (Fig. B 10-58) which are specially visible in Pt seals. In glass electrolysis in Dumet seals, the positive becomes blackened by O_2 production and hence CuO formation, while the negative either remains bright or the red Cu_2O layer often present becomes bright in spots by local reduction to Cu. In every case, throughout the life of the tube electrolysis produces at the glass-metal interface metals which, to an extent determined simply by the magnitude of the quan-

tity (current × time), reduce the bond between glass and oxidized metal seal wire or else cause cracks in the glass between the electrodes which are operative in the process.

2. Gases are released, mainly H_2, which worsen the vacuum. Analyses have revealed O_2, H_2O, N_2, CO and CO_2 as well ([1]GALLUP).

3. If the electrical conductance and the temperature are both high, the current flow can become sufficient to puncture and shatter the glass.



[10.2]

Fig. B 10-58 Glass-bead to metal-wire seal, using Pb-free sodium silicate glass; shown after prolonged electrolysis at high temperature ([1]KIRBY)

Positive electrode surrounded by large number of O_2-bubbles formed during electrolysis; negative electrode however is clear (the small bubbles were already present before the electrolysis as a result of the sealing process)

Electrical decomposition of glass can also be caused by A.C., since the current flows mostly in one direction, often because of rectifier effects, and the ions therefore also shift in a preferential direction. It has also been observed that this occurs between a single sealed-in electrode conductor and the surface of the surrounding glass if the latter is charged with stray electrons ([1]GALLUP).

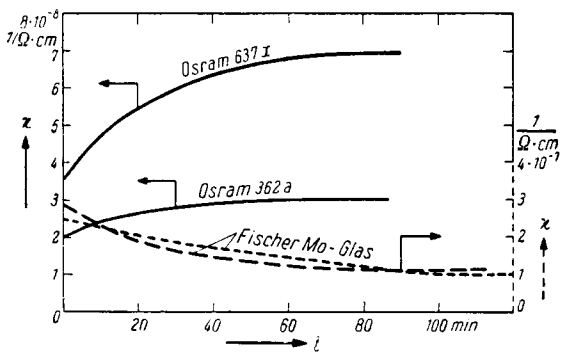


Fig. B 10-59 Electrical conductivity $\varkappa$ of technical glasses at 300° as functions of time t for which a 2000 V D.C. source has been applied

Under prolonged electrolysis (e.g. in a hot-running pinch), ions leave the oxidized electrode surface, or the glass itself can become locally depleted in ions after a time; these two effects can alter the conductivity in the positive or the negative sense (see, e.g., Fig. B 10-59). It is therefore a good procedure not to rely solely on absolute determinations of $T_{\varkappa 100}$ or on the ϱ value of the glass, but rather to make "life" tests on

prepared glass-metal seal models of a material *identical* with the one to be used as current conductors. On the assumption that the lifetime of such a device is determined solely by the product insulation leakage current × time of operation, for a given applied voltage, short-term tests at deliberately increased temperature (and therefore increased current) can often be used to determine what life can be expected under normal conditions for the glass, seal-geometry and applied voltage in question. (Cf. e.g. DÜSING.)

If a given pinch arrangement regularly cracks in operation of the tube after a certain
[10.2] time, one should first take constructional measures to lower the pinch temperature. For instance the neck of the envelope can be made longer or a radiation screen may be provided between foot and the working volume of the tube or an open, preferably air-cooled base cemented to the end. Curves of the temperature dependence of ϱ are shown in Fig. B 10-45, based either on direct measurements or on the $T_{\varkappa 100}$ point. They provide a means of estimating the necessary temperature drop for a suitable increased life of the pinch-foot. Naturally, there is no sense in obtaining a 10,000 hours life in a tube whose cathode only lasts for 2000 hours.

Should these steps not achieve a sufficient drop in temperature, it is necessary to use a glass of another type with better insulating properties, i.e. a higher $T_{\varkappa 100}$ point. Obviously there is no need to make the whole tube of highly insulating glass, and it is generally enough to make the parts which have specially exacting electrical requirements of this glass. A hot-filament lamp foot, which carries the leads and may run at 150–200°, can be made of lead glass which has relatively high insulation resistance while the bulb is a harder glass (e.g. lime magnesia silicate).

Electrolysis and the resultant glass discoloration can also arise from impact of fast electrons at the wall, as in electron bombardment of the picture screen of a cathode-ray tube, especially TV projection tubes, In such cases, Na, which has high mobility in electrolytes, is replaced by K, while BaO is added to the melt and also CeO_2, to reduce discoloration (see also Section 10.2.XVII and Table T 10–2, H). See also [2]ENGEL on this point.

See Chapter 25 for the technical use of glass electrolysis to introduce alkalis into photocells.

10.2.XII. *Surface Conductivity of Glass*

At temperatures below 100° the surface resistance of glass plays an important part as it may be many orders of magnitude less than the volume resistance. It is caused primarily by an absorbed water layer which completely disappears at temperatures somewhere above 100° (and is thus not the same as the water removed only above 400–500°, which comes from deeper layers and makes it essential to heat glass walls to over 400° during the process of degassing on the pumping system). The effect is shown by comparison of curves 3 and 4 in Fig. B 10-45. This water layer cannot be present in a tube that has been properly degassed by heat-treatment.[39] However, the skin of water on

[39] However, other conducting layers can have very harmful effects; e.g. evaporated electrode metals, stray getter deposits, etc., and even well-degassed quartz insulators in electrometer tubes lose their high insulation resistance if touched with bare fingers before or after assembly in the tube (BRONSON). See Chapter 27 for constructional methods of increasing the insulation of glass surfaces inside tubes, especially those with metal flash getters.

the outside can be very troublesome in sensitive electrometer tubes since its thickness increases markedly with the ambient moisture and therefore the conductivity increases (Fig. B 10-60, curves 1–5). It is necessary in such cases to keep the base dry with a

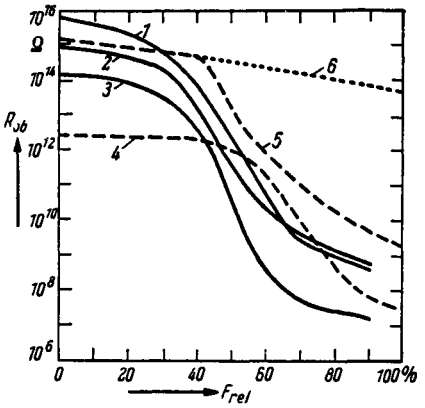


Fig. B 10-60 Superficial resistance R_{ob} of technical glasses, as functions of the relative humidity F_{rel}

1 Kavalier glass
2 German glass } from CURTIS
3 Window glass
4 Soda lime glass (Corning 0080)
5 Borosilicate glass (Pyrex 7740) } from [5]GUYER
6 idem, surface treated with silicone

[10.2]

connecting container of desiccant (e.g. P_2O_5). (See, e.g., Fig. B 10-61.) The effect of moisture on the surface conductivity can be considerably reduced by applying water-repellents (see Fig. B 10-60, curve 6). See Section 10.4.XIII for further details.

The surface conductivity must be taken into account as a source of error in the measurement of volume resistivity of glasses at temperatures below 100°. The simplest way to find the contribution of surface ϱ to total ϱ is to measure the resistance of a solid glass rod, the first time after heating to 300–400° and cooling in a dry space, and then after 15 minutes in a flow of water-saturated air. The difference in the two results gives the surface resistance, W_{ob}, and hence the surface resistivity, R_{ob}.[40] Measurements of R_{ob} of glasses of different compositions (Fig. B 10-62) show strong reduction of this parameter with increasing alkali content and also that certain limited amounts of additives, primarily CaO, B_2O_3 and BaO, can raise the surface resistivity considerably.

On the other hand, a certain degree of surface conductivity in glass can often be desirable in tube construction, but it must obviously not depend on

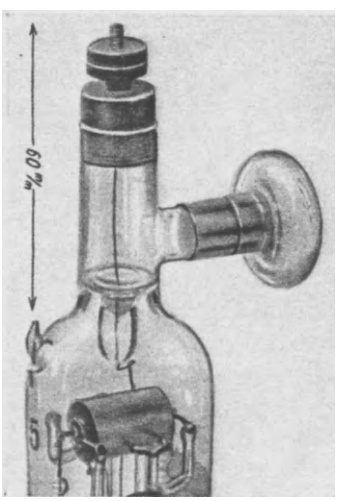


Fig. B 10-61 Reduction of the conductivity of the external surface of an electrometer tube by drying the base with P_2O_5 and sealing up with an amber plug ([1]SIEMENS)

[40] R_{ob} is defined without reference to the unknown and variable film thickness by:

$$R_{ob} = \frac{W_{ob} \cdot l}{u} \quad \left(\Omega \frac{\text{cm}}{\text{cm}}\right) \quad \text{or} \quad (\Omega),$$

where l is the length of the solid glass rod tested and u its circumference, both in the same units, e.g. cm. The surface resistivity R_{ob} is thus the resistance of a conducting film 1 cm long and 1 cm wide which is also the resistance of a square of arbitrary side (so-called "resistance per unit square").

uncontrolled variables like the moisture content of the air, and its magnitude must be precisely fixed. Additions of Bi-, Pb-, and Sb-oxides can be made to the glass and the surface can be reduced by slow heating in H_2 from 350 to 520° (GREEN, [1]BLODGETT) to achieve the desired effect. This process will produce dark, conducting layers of *ca.* 25 μ thickness, whose R_{ob} may fall to about 100 MΩ at room temperature. For details see Sections 10.4.X and XI.

[10.2]

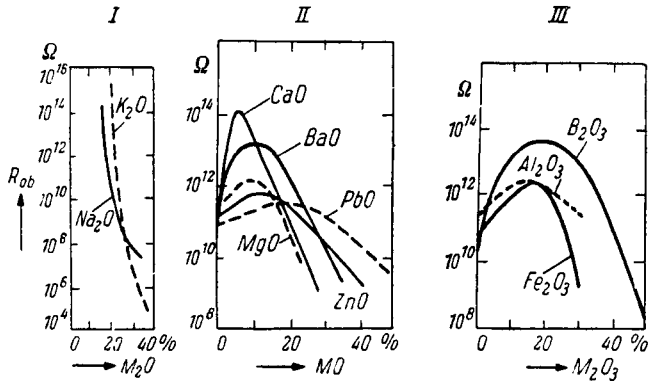


Fig. B 10-62 Superficial resistance R_{ob} of ternary silicate glasses as functions of their composition (FULDA)
I lead sodium-silicate glasses with constant PbO content (20%), and varying alkali content M_2O; II and III sodium-silicate glasses with constant Na_2O content (18%) and varying content of another oxide MO or M_2O_3

10.2.XIII. *Dielectric Constant ε and Dielectric Loss Angle tan δ (Dielectric Loss Factor $\varepsilon \cdot \tan\delta$) of Glasses*

When current leads and electrodes are fed with A.C., and glass in any form is present between them (particularly therefore metal leads sealed into glass), a capacitor is formed with glass as the dielectric. The power loss is well known to be

$$N = U^2 C_0 \cdot 2\pi \nu \cdot \varepsilon \cdot \tan\delta \quad \text{(watt)},$$

where U (V) is the applied voltage, C_0 the capacitance without dielectric, and determined by the geometry, ν (c/s) the frequency of the applied voltage, ε the dielectric constant of the glass and δ the loss angle. At low frequencies and voltages this loss is of no importance, but in transmitter tubes with high voltages and frequencies the dielectric loss at certain heavily loaded areas can be sufficient to cause local heating of the glass to such an extent that the softened glass is forced inwards by the external air pressure (so-called "Ausbläser" in German) (see, e.g., KUSUNOSE). Since ε and also $\tan\delta$ to an even greater extent, depend on glass composition, temperature and applied frequency, these electrical parameters must be kept as low as possible in such applications, and their temperature and frequency dependence must be determined; this is quite apart from constructional measures such as increasing the distance between the electrodes, additional cooling, and screening of the areas of glass concerned.

Dielectric constant ε of glasses. There is an empirical relationship between the density γ (g/cm^2) and ε:

$$\varepsilon \approx 2.2\,\gamma$$

as shown by Fig. B 10-63. The lowest values of density and hence of ε are those of high boron glasses and quartz, varying between 3.5 and 4.

ε rises with temperature, particularly at low frequency, but at the higher frequencies (which are of more interest) and for values below 5, the variation is small as shown in Figs. B 10-64 and B 10-65 (see also Figs. B 10-66 and B 10-67, curve for 7070 glass). As ν rises, ε drops only slightly, as shown in Figs. B 10-66 and B 10-67.

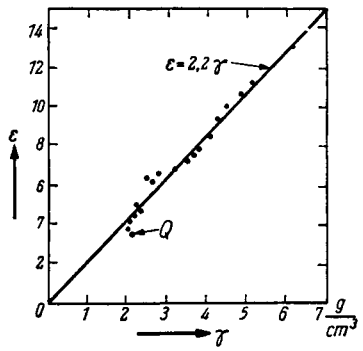


Fig. B 10-63 Dielectric constant ε of technical glasses at room temperature as a function of the density γ (Q quartz glass)

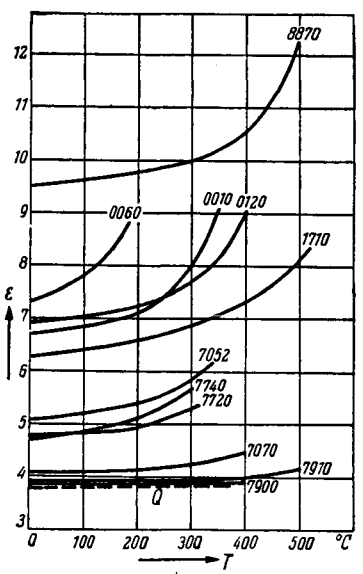
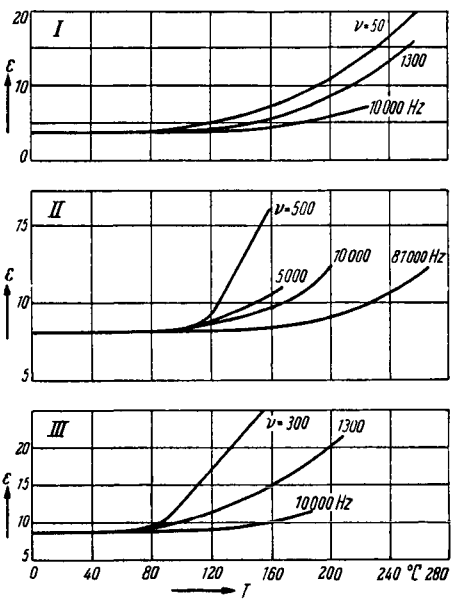


Fig. B 10-65 Dielectric constants ε of Corning glasses at 1 Mc/s as functions of temperature T (from [1]CORNING) (cf. also Table T 10-4, A 1). Q quartz glass



[10.2]

Fig. B 10-64 Dielectric constants ε of three glasses as functions of temperature T for various frequencies ν (from [2]STRUTT)

I Pyrex-type glass; II 70% SiO_2, 16% Na_2O; III heavy Pb-glass

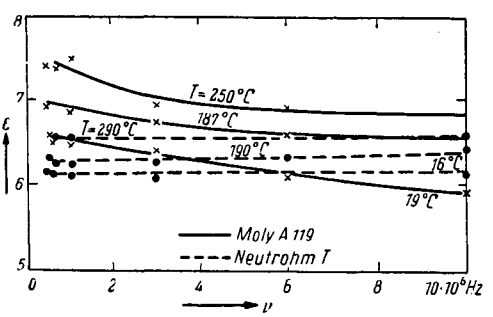


Fig. B 10-66 Dielectric constants ε of two French glasses for various temperatures T as functions of frequency ν (from MEUNIER)

Loss angle tan δ. In the temperature range above room,[41] this parameter rises strongly with temperature according to:

$$\tan\delta = A\, e^{kT}; \quad \log(\tan\delta) = C + kT,$$

where T (°K) is temperature, and A, k, and C are constants, as shown in Figs. B 10-68, B 10-69, B 10-70 and B 10-70A. However, the increase is less at high frequencies (see Fig. B 10-70, right-hand diagram and B 10-70B).

[10.2]

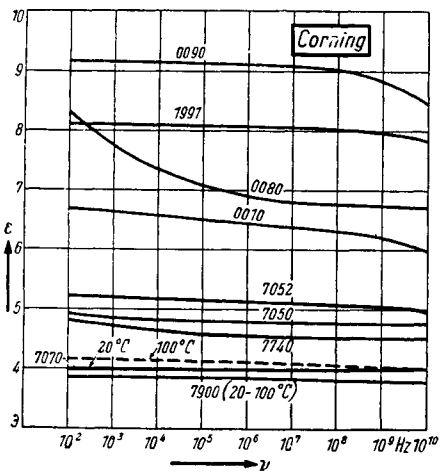


Fig. B 10-67 Dielectric constant ε of Corning glasses as a function of frequency ν

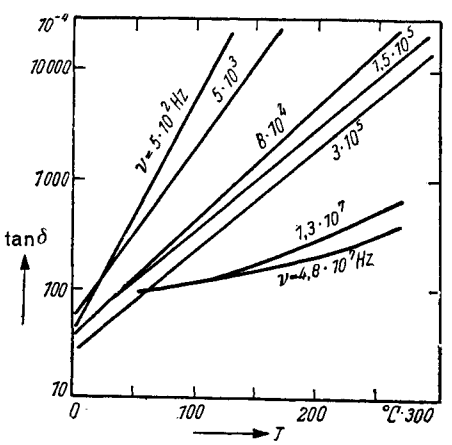


Fig. B 10-68 Dielectric loss angle (tan δ) of a sodium silicate glass at various frequencies ν as a function of temperature T (from [1]STRUTT)

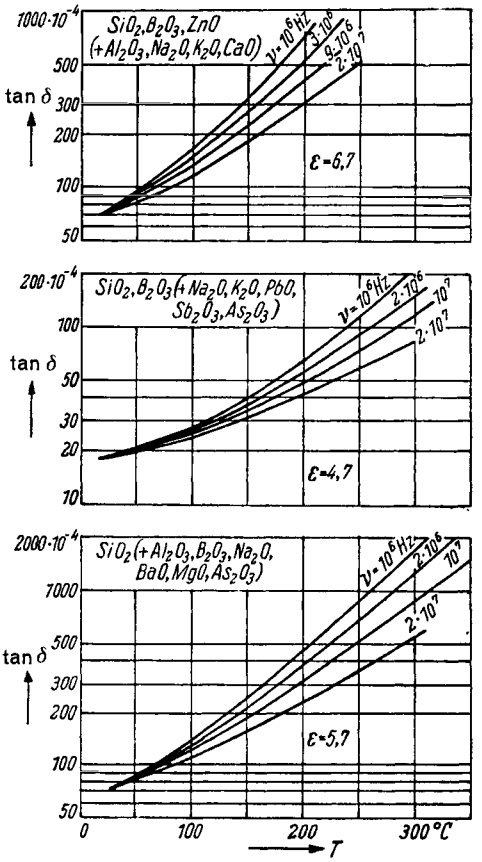
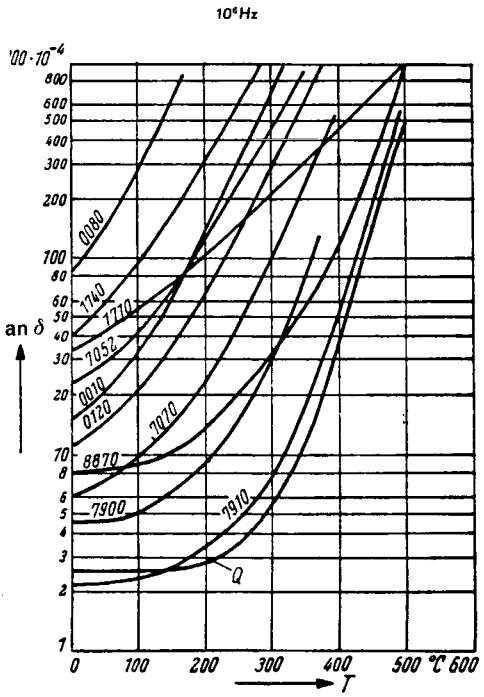
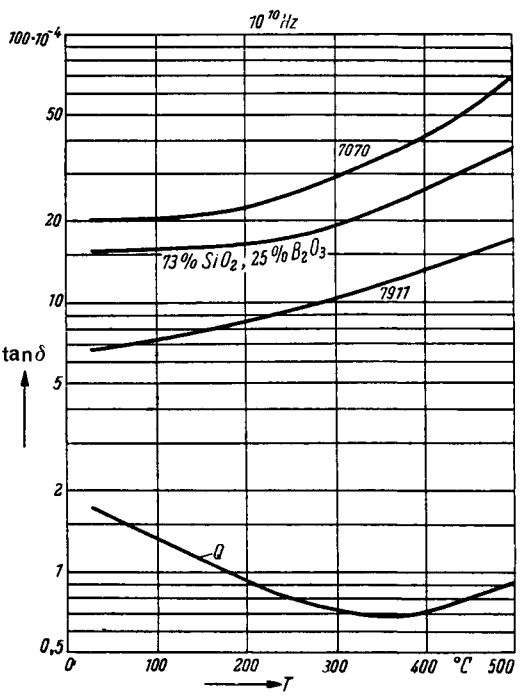


Fig. B 10-69 Dielectric loss angle tan δ of three glasses (free of water layers for various frequencies ν as temperature T functions (from [1]STRUTT)
ε= the dielectric constant in each case

[41] It should be noted that at temperatures below 0 °C, tan δ often rises again, so that the T-dependence like the ν-dependence, shows a minimum (see Figs. B 10-71, B 10-72 and B 10-70A), provided one considers a wide enough range of T; see, e.g. GEVERS and especially [5]STEVELS, who has set up a basic and complete three-dimensional model of frequency-temperature-tan δ for $\nu = 10^2$ to 10^{12} c/s and $T = 0-600$ °K.





[10.5

Fig. B 10-70 Dielectric loss angle tan δ of Corning glasses at 10^6 and 10^{10} c/s as functions of temperature T (from CORNING) (see also Table T 10–4, A1). See MILLER for corresponding measurements at 60 c/s

Q quartz glass; Corning 7052 and 7720 have the same tan δ curves

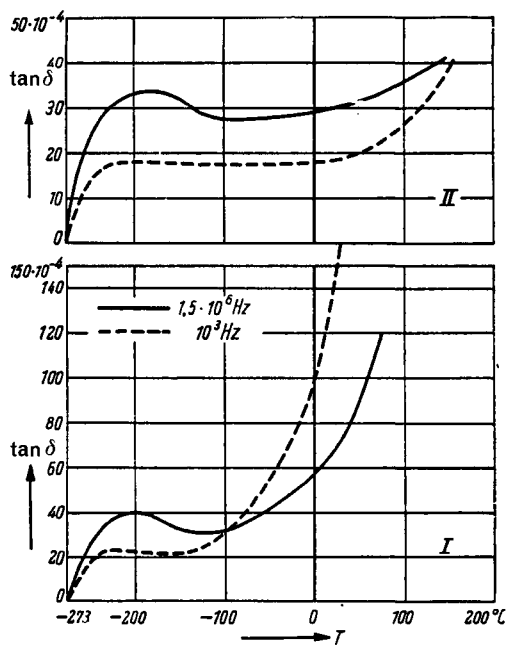


Fig. B 10-70 A (Right) Dielectric loss angle tan δ of a soft soda-lime glass I and a hard borosilicate glass II at very low temperatures for various frequencies ν as functions of temperature T (5STEVELS)

Compositions in $w/_0$ are as follows:

GLASS	SiO_2	B_2O_3	Al_2O_3	Na_2O
I	70.7	–	0.5	16.8
II	57.5	4	21.5	–
GLASS	K_2O	CaO	MgO	BaO
I	1	5.5	3.5	2
II	0.4	6.3	9.3	1

[10.2]

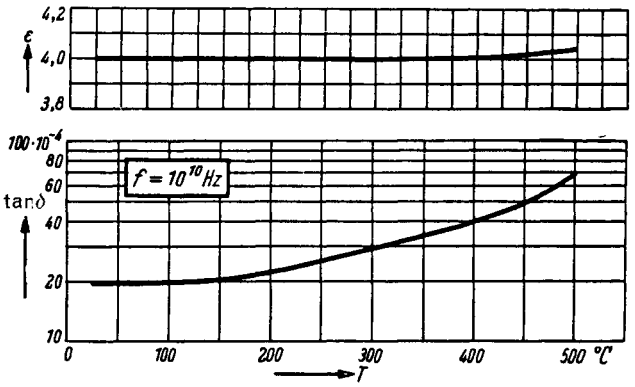


Fig. B 10-70 B Dielectric constant ε and loss angle tan δ of a low-loss borosilicate glass, Corning 7070, as functions of temperature T at 10^{10} c/s (HIPPEL)

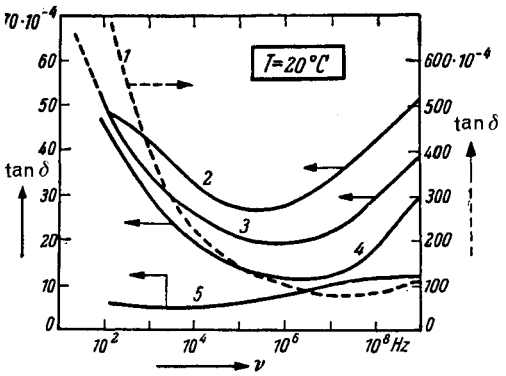


Fig. B 10-71 Dielectric loss angle tan δ of a few typical glasses at room temperature as functions of frequency ν ([1]STANWORTH). All curves except *1* are referred to the left-hand ordinate

1 soda-lime glass with 17% Na_2O (right-hand scale); *2* alkali-free aluminosilicate glass; *3* borosilicate glass; *4* lead glass; *5* low-loss borosilicate glass

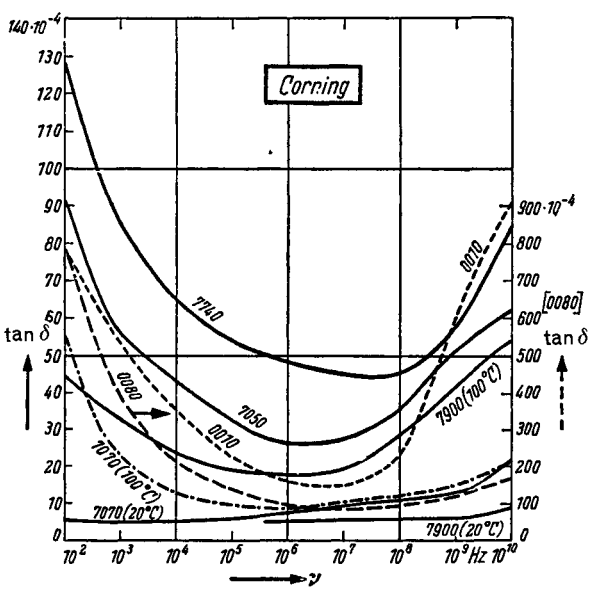
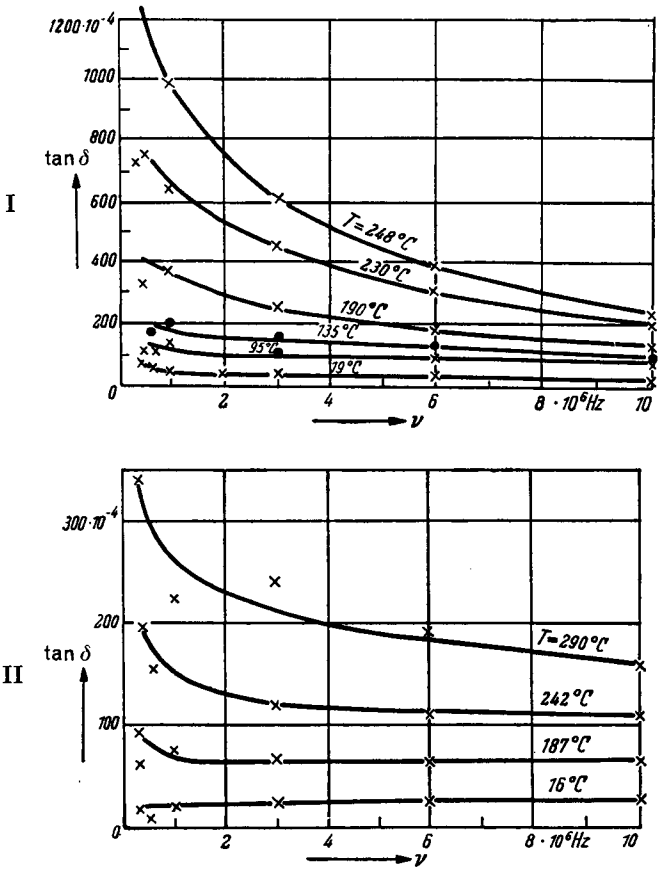


Fig. B 10-72 Loss angle tan δ of Corning glasses as functions of frequency ν (CORNING). Obtained at room temperature where not otherwise stated. For all curves except the 0080 glass use left-hand ordinate (see also Table T 10–4, A 1, and [5]GUYER); cf. Fig. B 12-32



[10.2]

Fig. B 10-73 Loss angle tan δ of two French glasses as functions of frequency ν for various temperatures T (MEUNIER)

I Moly A 119 glass; II Neutrohm T glass

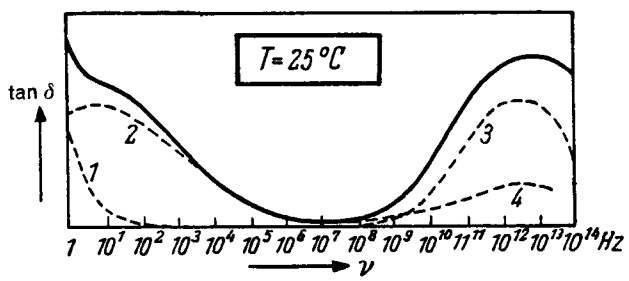


Fig. B 10-73A Schematic representation of the frequency spectrum of dielectric loss in glass at room temperature ([5]STEVELS)

The solid curve gives the overall losses, from which it can be presumed that they are composed of *1*, the conduction loss; *2*, the relaxation loss; *3*, the vibration loss and *4*, the deformation loss

The frequency-dependence of $\tan\delta$ for glass generally shows a definite minimum between 10^5 and 10^6 c/s (see Figs. B 10-71 and B 10-73).

When the dependence of $\tan\delta$ on composition is in question, it must be borne in mind that the dielectric losses come about because of the mobility of glass molecules in the alternating electric field, and this uses energy which appears externally as heating of the glass. These losses can arise from movement of the modifier ions[42] or from distortion of the silicate lattice itself ("distortion or deformation losses") (see Fig. B 10-73A). While only the second occurs in pure quartz without modifiers (resulting in very low losses), the addition of modifiers in ordinary silicate glasses loosens the strong bonds of the Si—O—Si chains so that the losses increase; here three types of ions can be clearly distinguished:

[10.2]

1. high mobility ions, mainly Li^+ and Na^+, since they have the smallest diameters; $\tan\delta$ is thus smaller when fewer mobile ions[43] are present;
2. low mobility ions, e.g. K^+ and Mg^{++} (K^+ because of its large diameter compared to Na^+, Mg^{++} in spite of its double bond is still fairly mobile because of its relatively small diameter);
3. immobile ions, e.g. Pb^{++} and Ba^{++} (large diameter, divalent).

Systematic research (see, e.g., BOGORODITSKY, [1]HOOD, LYSENKO, NAVIAS, [2,3]STEVELS, [1]WEYL) has now shown that $\tan\delta$ can be reduced by the following means:

(a) Recombination of mobile with immobile ions. This is the case for alkali-silicate glasses containing about 30% PbO. The large immobile ions act as brakes on the high mobility of alkali ions just as in D.C. conduction processes, by blocking their motion from one interstitial position to the next.

(b) Mutual interaction between mobile ions, or between immobile ions, but of different diameters. For example, in sodium-silicate glasses, the Na^+ ions are replaced partly by Li^+ ions, or by K^+ or Mg^{++} ions and $\tan\delta$ is thereby reduced (see Fig. B 10-74). If Na ions are replaced by Zn ions, this effect does not occur, as the ionic diameters are nearly the same.

At first sight this is very surprising because Li^+ ions are much more mobile than Na^+ ions and therefore glasses which contain large amounts of Li_2O actually have a larger $\tan\delta$ than equivalent Na_2O glasses. The explanation of the reduction in $\tan\delta$ is to be sought in the fact that Li^+ ions present in small amounts lead to a contraction of the lattice and only when present in large amounts does their high mobility come into play (see Fig. B 10-74). When replacing Na^+ ions by K^+ ions with their much larger ionic diameter, the optimum ratio Na_2O/K_2O lies between 1:1.5 to 1:4. Figure B 10-75 shows this by the example of a glass with 45% SiO_2,

[42] These ions move through the whole network of the glass ("conduction loss", only noticeahle at very low ν) or else they jump from one interspace to another ("relaxation losses", in the range helow 1 Mc/s); or they may oscillate ahout their lattice positions ("vibration loss", in the range ahove 10^7 c/s). Figure B 10-73A gives a schematic presentation of the hehavior of an individual particle and thus of the overall loss throughout a frequency spectrum of $1–10^{14}$ c/s at a room temperature ([5]STEVELS).

[43] It should he horne in mind here that mobile ions like Na in small amounts may also hecome immohile; see further helow.

32% PbO, 5% CaF_2 and 18% (Na_2O + K_2O), where the optimal ratio for the least tan δ value is about 4:14 = 1: 3.5.

By and large therefore, it is the rule that modifiers of dissimilar mobilities affect each other so as to produce a reduction of energy absorption in the H.F. field. Modern low-loss glasses use a combination of Li_2O, Na_2O and K_2O.

(c) By introduction of small quantities of mobile ions into the specially restricted interstitial gaps in the lattice, which are always present even if in small numbers. The ions are bonded tightly here so that properties arising from their large mobility [10.2]

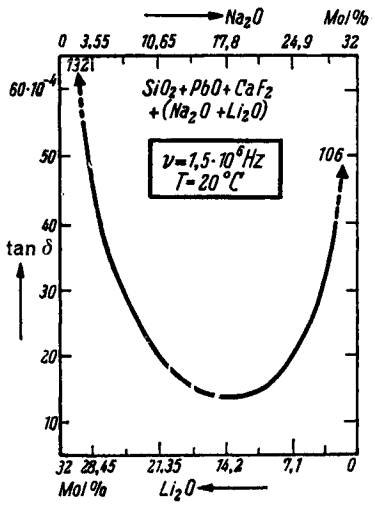


Fig. B 10-74 Dielectric loss angle tan δ of a series of glasses of the type: 53.3 mol. % SiO_2 + 10.2 mol. % PbO + 4.5 mol. % CaF_2 + 32 mol. % (Na_2O + Li_2O), in which the mol. % ratio of Na_2O to Li_2O is varied continuously. The tan δ minimum is at about 14 mol. % Li_2O : 18 mol. % Na_2O ([3,4]STEVELS)

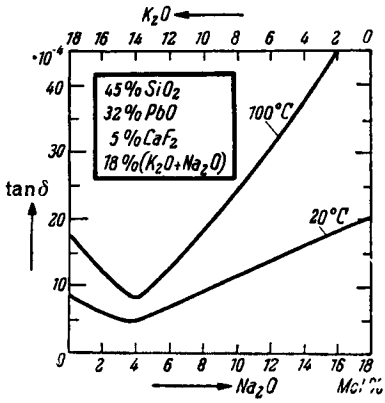


Fig. B 10-75 Dielectric loss angle tan δ at 20° and 100° of a series of glasses of the type: 45% SiO_2, 32% PbO, 5% CaF_2, 18 mol. % (Na_2O + K_2O) in which the ratio Na_2O : K_2O is varied continuously. The minimum tan δ occurs for about 4% Na_2O : 14% K_2O ([1]STEVELS)

are absent. It follows that the amounts introduced must not exceed a certain limit and glasses with pronounced low-loss characteristics never contain more than 3% Na_2O, but lead glasses may have over 5%. Otherwise, if the Na_2O content is higher, the alkali ions occupy the large interstitial gaps also, where they are only loosely bonded and so have normal mobility, in which case tan δ is increased again as the alkali content rises. Furthermore, the better a glass is annealed by suitable thermal treatment and slow cooling, the more readily the ions achieve stable groups; this is an informal explanation of the known fact that poorly annealed glass has much higher losses (up to three times) than well-annealed material, a point to consider especially in USW tube glass-metal seals (power-output windows).

B_2O_3 has a special position among glasses with low losses. In pure form as the only lattice component, with strong B—O bonds, it permits no relaxation mobility of the

ions in an A.C. field, and hence, as appears in curve I of Fig. B 10-76, exhibits very low $\tan\delta$, less than 10×10^{-4}. The B—O interatomic spacing is less than that of Si—O, and its size militates against the movement of alkali ions when it is added to silicate glasses. For the same reason, if large amounts of alkali are introduced into borate glasses without SiO_2 content, the loss angle $\tan\delta$ remains relatively small at room temperature (see Fig. B 10-76, curves II and III). Therefore, in the case of glasses with high SiO_2 content and correspondingly high viscosity, it is better from the point of view of dielectric losses to reduce the viscosity with large B_2O_3 additions than with alkali,
[10.2] and the alkali content can thus be reduced to 3–5%. At the same time, such glasses have low density because of the lack of heavy ions (PbO), and hence a low ε-value; the loss factor $\varepsilon\cdot\tan\delta$ is correspondingly small.

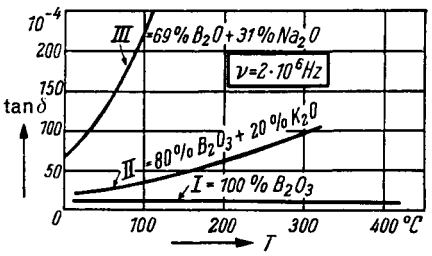


Fig. B 10-76 Dielectric loss angle $\tan\delta$ of glassy B_2O_3 and alkali borate glasses without SiO_2 content, measured at 2 Mc/s, as a function of temperature T (see also BOGORODITSKY)

The Si—O bond is strong, and therefore naturally the $\tan\delta$ of pure quartz and Vycor glass (96% SiO_2, with small amounts of B_2O_3 and Na_2O) is very low, $2\text{–}3\times10^{-4}$ and *ca.* 5×10^{-4} respectively.

In practice, it is therefore generally possible to distinguish two groups of commercial glasses with low dielectric loss:

(a) glasses with high Pb and low alkali content, which unfortunately have a high ε (7–8); examples are the SCHOTT glass Minos, and 3079^{III} (analysis in Table T 10–2, D 9); another is MOOSBRUNNER glass W 2 (analysis in Table T 10–2, Oe);

(b) borosilicate glasses with B_2O_3 content above 20% and low alkali content with $\varepsilon = 4\text{–}5$; examples are CORNING glass 7070 (analysis in Table T 10–2, A 1) and ČSSR low-loss glass K 707 (analysis in Table T 10–2, C).

The ε and $\tan\delta$ values of the best-known glasses for vacuum work are given in property tables (Table T 10–4), with temperature and frequency dependence, and references to text-diagrams.

It is often necessary in the application of low-loss glass to reduce dielectric loss in H.F. tubes by special constructional methods. First of all, one must avoid taking several H.F. voltage-carrying leads side by side through the glass too near together, e.g. through the same pinch; this means keeping the lead capacity C_0 low (cf. the formula for power loss at beginning of Section 10.2.XIII). In the short-wave transmitter tube of Fig. B 11-12, anode and grid leads are fed through two widely separated seals. Under certain conditions (e.g. restricted assemblies in short-wave tubes) it is generally no longer possible to use glass as a constructional material inside the tube, as it would

soften under the heat radiated from anode and cathode and from dielectric loss; this is taken into account in the tube shown in Fig. B 11-12: the grid structure is not supported, as is otherwise usual, by the glass to which the pinch carrying the cathode leads is fused, but is supported by quartz rods Q_1 or insulators of low-loss ceramic (see Chapter 12). The upper portion of the grid is held together by a quartz crown Q_2. Ordinary glass in this position would soften in a short time. A similar construction of top bridge in a smaller transmitter tube is shown in the right upper corner of the figure mentioned.

A low loss-angle is particularly important for power-output windows of UHF tubes [10.2] (magnetrons, klystrons). Round windows of CORNING 7070 (Table T 10–4, A1 suppl. II, Figs. B 10-70, B 10-70B) 20 mm diameter and 1.2 mm thick will pass 300 W of H.F. at wavelengths of 3 cm and less ([1]DORGELO); the window will not soften from the energy absorbed and thus will not cave in under atmospheric pressure, provided there are no standing waves caused by mismatch.

10.2.XIV. *Electrical Breakdown Strength of Technical Glasses*

([1]GEHLHOFF, MOREY, [1]SHAND)

The electrical breakdown or rupture strength E_d is usually given in kV/cm and is therefore the breakdown voltage in kV for 1 cm thickness. At room temperature and with ordinary glass, it is usually so high that flashovers in air between the electrodes or a creeping discharge along the glass surface of the seal area are more likely than a breakdown through the glass between leads. However, as the inside of a well-degassed HV tube lacks the conducting (water) surface layer which normally forms in the atmosphere, static charges can build up on the internal surface of the glass envelope of high vacuum-high voltage tubes (e.g. X-ray tubes). These charges stress the glass strongly in a direction normal to the wall surface and may lead to pinholes.[44] Extended striae are a special hazard in this case and so above all are gas bubbles in the wall, because, due to the different dielectric constants (glass 5–16, air 1), field concentrations occur which can rise to the point where the gas sealed in the bubble is ionized. This makes possible the complete rupture of the wall. It is therefore an extra requirement for glass in HV tubes that it be extremely bubble-free.

The breakdown voltage parallels the electrical resistance as a rule, and is thus greatest for borosilicate glasses and least for alkali-silicate glasses (Fig. B 10-77), It depends very much on surface condition and on the type of surrounding medium; air, oil, etc. (see Fig. B 10-77A). It rises less than linearly with thickness d so that the strength falls off at greater thicknesses if calculated on the constant thickness of 1 cm (see, e.g., Fig. B 10-78). If the strength is related to constant thickness but measured at varying temperatures, there are clearly two temperature ranges to distinguish (Fig. B 10-79):

(a) a lower one, the disruptive breakdown range in which E_d is substantially independent of temperature, and in which no rise in temperature occurs before rupture due

[44] This type of tube therefore is made with a glass of deliberately lowered electrical resistivity (see Table T 10–4, A 3) or else the glass is provided with a stable layer which is slightly conducting (see Sections 10.4.X and XI and also [1]BLODGETT, GREEN).

to electrical stress; rupture takes place at a definite field strength where the ionic bonds in the lattice are broken;

[10.2]

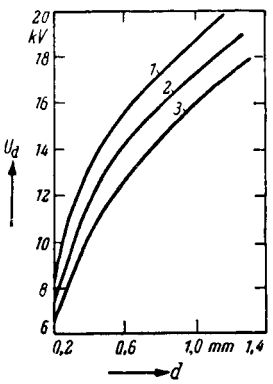


Fig. B 10-77 Breakdown voltage U_d for various types of glass as a function of thickness d (RETZOW)

1 borosilicate glass; *2* alkali-free glass; *3* normal alkali glass

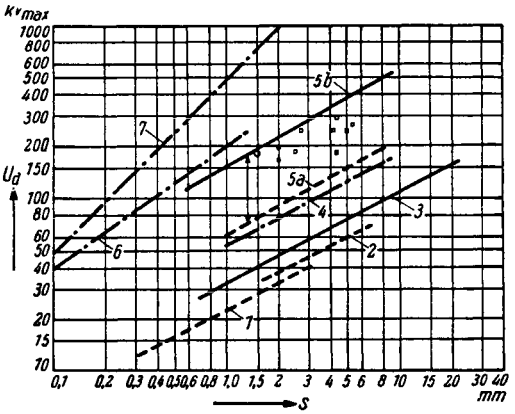


Fig. B 10-77A Breakdown voltage U_d (peak values) of various glasses with different surface conditions as a function of the wall-thickness s ([1]SHAND)

1 soda-lime glass under oil; *2* mirror glass under oil; *3* Pyrex glass disks under oil; *4* Pyrex glass disks under special, high-insulation resistance oil; *5a*-*5b* Pyrex glass in air; *6* Pyrex glass, normal breakdown, no edge effect; *7* Pyrex glass, true breakdown voltage

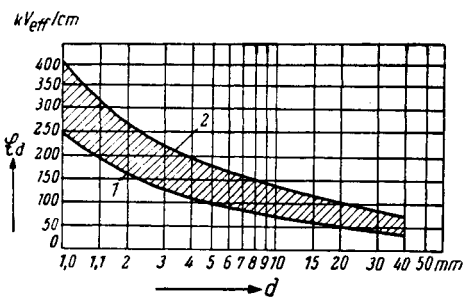


Fig. B 10-78 Electrical breakdown strength E_d at 20° of Pyrex glass 7740 as a function of thickness d. Measured at 60 c/s and voltage rise rate of 670 V/sec ([7]ESPE)

Curve *1* under oil; curve *2* in air

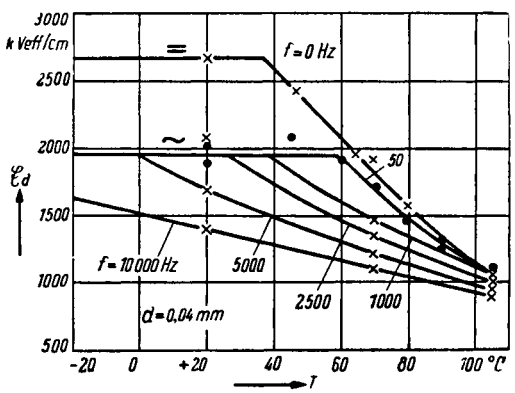


Fig. B 10-79 Breakdown strength E_d of glass of thickness $d = 0.04$ mm as a function of temperature T, measured at various frequencies f

(b) a higher, so-called thermal breakdown range in which, because of the very strongly negative temperature coefficient of electrical resistance and the poor thermal conductivity, an increase of temperature and electrical conductance (each increasing the other) occurs (Fig. B 10-79A), until finally both become so large in a restricted

current path that breakdown follows. Pure electrical breakdown takes place mainly through thin walls and as a result of short-term stress, but thermal breakdown occurs in thick walls where heat cannot escape so easily.

At the higher frequencies, breakdown strength falls as frequency rises (Figs. B 10-79, B 10-79B, and B 10-80), since the glass is heated by the additional dielectric loading, the more so the higher the frequency.

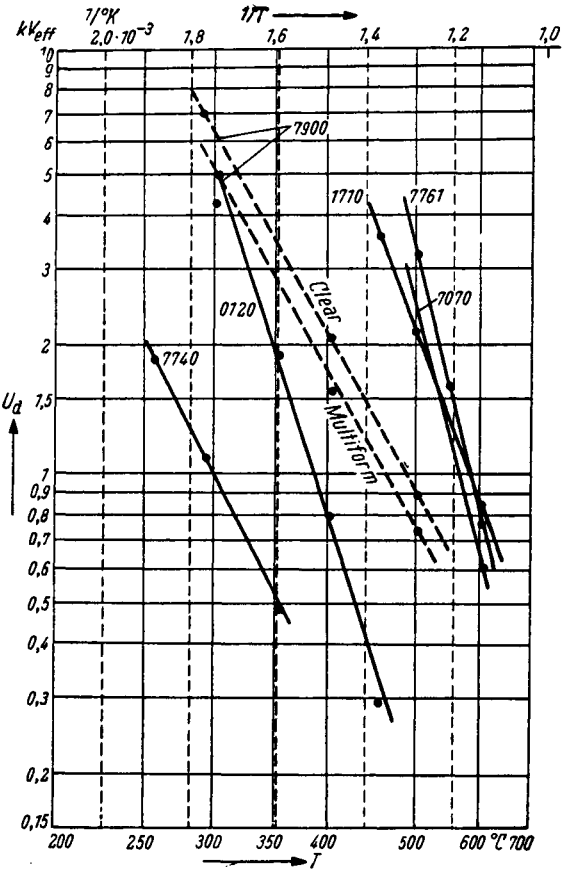


Fig. B 10-79A Breakdown voltage U_d of different Corning glasses as functions of temperature T (3SHAND)

Test-piece thickness: 2 mm, test voltage: 60 c/s. For 7900 glass two curves: "clear" and "Multiform" (sintered)

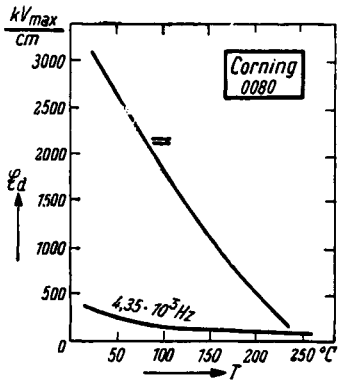


Fig. B 10-79B Breakdown strength E_d of a soda-lime glass (Corning 0080) as a function of temperature T, with D.C. applied voltage and with H.F. voltage at 4.35×10^5 c/s (5GUYER)

[10.2]

Methods of construction used to prevent breakdown are chiefly: enlarging and cooling the glass envelope, use of borosilicate glasses possibly with increased volume or surface conductivity, walls not too thin, and screening of the outer glass wall from direct bombardment by stray electrons (see, e.g., Fig. B 10-81). Creeping surface discharge can easily lead to destruction of the glass and one can guard against it either by immersing the whole tube in oil or by corrugating the glass wall (Fig. B 10-82).

[10.2]

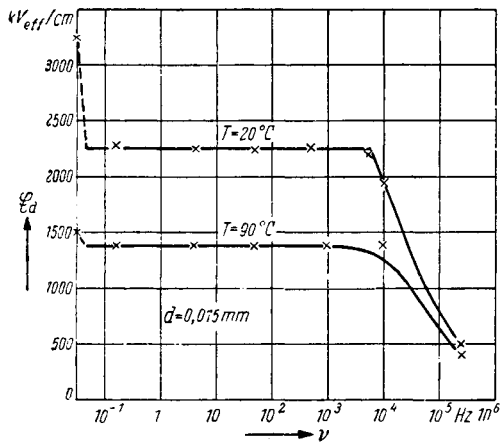


Fig. B 10-80 Breakdown strength E_d for glass of thickness $d = 0.015$ mm, as a function of frequency ν for various temperatures T

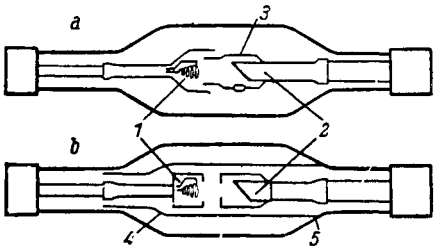


Fig. B 10-81 Prevention of charges caused by electron bombardment of the glass wall in high-voltage tubes (e.g. X-ray tubes). Schematic illustration based on products by SIEMENS-REINIGER-WERKE (cf. also [2]SIEMENS)

a metal screening tube; *b* glass screening tube: *1* cathode; *2* anode: *3* metal screen (also acts as radiation screen); *4* glass screen; *5* fusion joint area

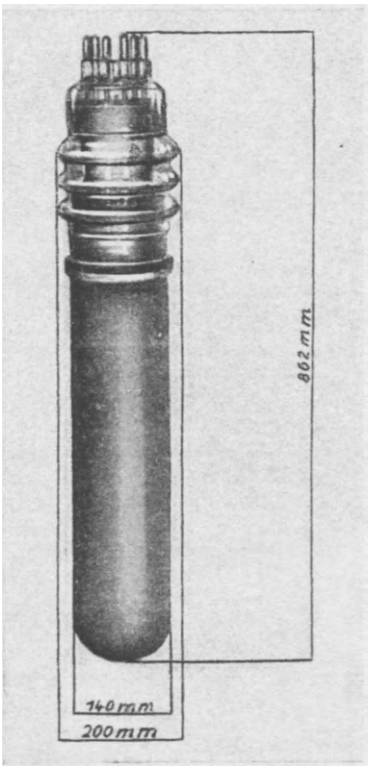


Fig. B 10-82 Increasing the dielectric strength of a transmitter tube with 18 kV plate voltage by corrugating the glass tube section, which is sealed at one end to the anode and at the other to the cathode-grid system (Manufacturer: SFR)

10.2.XV. *Permeability of Technical Glasses to Gases*

(DUSHMAN, [1]STANWORTH)

Glass is virtually impermeable to all gases except He, which will diffuse at elevated temperatures through silicate glasses in detectable quantities (see Table T 10–8 A). In ultra-high vacuum glass systems, pressure rises at 20° can be observed, amounting to 5×10^{-12} Torr/sec, which are attributed to the permeability of the glass to He (ALPERT). The gas appears to permeate gaps in the lattice of the structural components (Si, B, P) of the glass. Permeability ξ is therefore reduced by blocking the seholes with Na, K or Ba ions, and is increased by raising the content of SiO_2, B_2O_3 and P_2O_5 (Fig. B 10-82 A and B). ξ is therefore largest in pure quartz (see Chapter 11, esp. Table T 11–4 and Fig.

TABLE T 10-8A. PERMEABILITY ξ OF SILICATE GLASSES TO He (RESULTS FROM BARRER WHERE NOT OTHERWISE STATED); CF. ALSO FIG. B 10-82D

TYPE OF GLASS	T(°C)	$\xi \left(\frac{cm^3(NTP)\cdot mm}{s\cdot cm^2\cdot Torr}\right) \times 10^{-13}$
Thüringer glass	300	0.84
Jena glass 16III	300	3.6
Lead-silicate glass	283	3.7
Sodium-silicate glass	283	9.8
Borosilicate glass	300	380
	600	1900 (1)
Quartz glass	300	3150

[10.2]

(1) GMELIN.

B 11-11). ξ rises with temperature (Fig. B 10-82B to D), according to the expression

$$\xi = A\, e^{-B/T}, \quad \text{or} \quad \log \xi = C - D(1/T),$$

where A, B, C and D are constants and T is the absolute temperature (°K). Permeability ξ is defined by the equation

$$\xi = v \cdot d/O \cdot t(p_1 - p_2) \quad (\text{cm}^3\,(\text{NTP}) \cdot \text{mm/cm}^2 \cdot \text{sec} \cdot \text{Torr}),$$

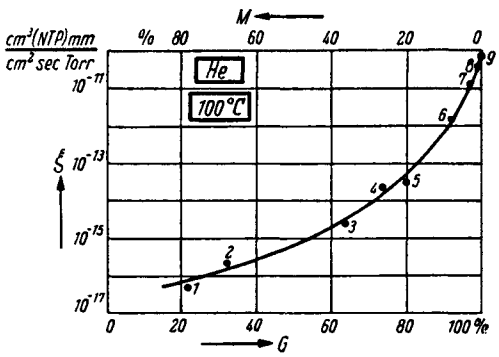


Fig. B 10-82A Permeability ξ for He of various glasses at 100° as a function of total amount of glass-forming components ($SiO_2 + B_2O_3 + P_2O_5$) (3NORTON)

The numbers by measured values refer to glass types given in Fig. B 10-82D

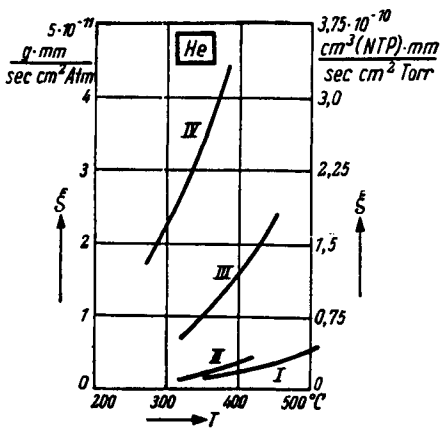


Fig. B 10-82B Permeability ξ to He of technical glasses as temperature (T) functions (SMITH)(1)

I soda-lime glass (73% SiO_2, 17% Na_2O, 5% CaO); *II* lead-silicate glass (62% SiO_2, 23% PbO); *III* borosilicate glass (61% SiO_2, 29% B_2O_3); *IV* Pyrex glass (*ca.* 81% SiO_2, 12% B_2O_3)

(1) 1 g He = 5.6×10^3 cm³ (NTP) He.

where v (cm³ NTP) is the amount of gas which diffuses through the glass, reduced to 20° and 760 Torr, d (mm) is the glass thickness, O (cm²) is the glass surface exposed, t (sec) is the time in which diffusion takes place, and p_1 and p_2 (Torr) are the pressures of gas at entrance and exit from the glass respectively.

The gas permeability for various gases drops (if secondary effects with H_2 are neglected) as the atomic radius of the diffusing gas increases (see also Table T 11–4). For example, the Ar permeability of Pyrex from 390 to 450° is $1/10^5$ of that for He in the same temperature range (W. A. ROGERS). The H_2 permeability of CORNING ignition glass 1720 was found to be 4.5×10^{-13} at 665°, and the value for He under the same experimental conditions was 300×10^{-13} (units as above) ([3]NORTON).

10.2.XVI. *Transmission in the Visible, IR and UV Spectral Range*

[10.2]

The transparency of a glass is one of the most important properties in technical work. Standard, untinted, Fe-oxide-free, clear glass absorbs between 6 and 20% of visible light, usually 10%; this is for vacuum vessels of normal thickness, 1—2 mm. Only a small part of this is true absorption, the rest being reflection loss at both surfaces of the glass (about 4% per surface). The errors this makes

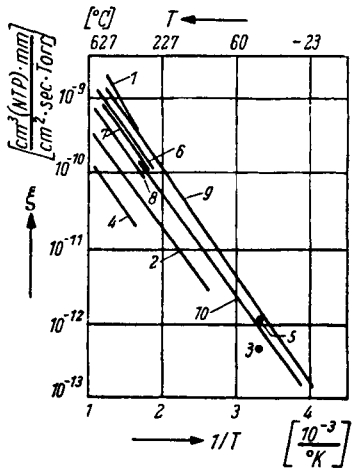


Fig. B 10-82c Permeability ξ (cm^3 NTP · mm/cm^2 · sec · Torr) of Pyrex 7740 for He as a function of the reciprocal of absolute temperature ($1/T$)
A collection by ROGERS of measurements of different authors

TABLE T 10-9. CORRECTION $+\Delta T$ TO PYROMETRIC MEASUREMENTS OF T_w, THE TRUE TEMPERATURE OF ELECTRODES; THIS CORRECTION TAKES ACCOUNT OF REFLEXION AND ABSORPTION OF RADIATION BY ORDINARY GLASSES BETWEEN THE SOURCE AND THE PYROMETER (FOOTE)

T_w (°C)	CORRECTION, $+\Delta T$ (°C)
600	3.5
800	5.4
1000	8
1200	10
1400	13
1600	16
1800	20
2000	24
2500	36
3000	50

in pyrometric measurements are small. They can be corrected by adding a few degrees to the temperature measured, as given in Table T 10–9. The error is only 8° per 1000°, as can be seen.

Weathering can lower the transparency of soda-lime glasses up to 8% (STOCKDALE).

Soda-lime, lead and borosilicate glasses can be tinted by introducing metal oxides which can be suspended or dissolved in the basic glass without needing to alter the other properties or the composition. For example, Fe_2O_3 colors glass yellow-green; FeO, green-blue (see Fig. B 10-82 E). Glass with Cr_2O_3 additions first transmits yellow-green light and then deep red (see Fig. B 10-82 F), while the blue and violet rays are strongly absorbed. Cadmium oxide colors glass yellow; cobalt oxide, blue. There are specific absorption bands for the individual oxides whose position shifts as the basic

glass composition alters. Table T 10–10 is a collection of the chief oxides used to color glass. Colored glass is employed in vacuum work for therapy, photography, and indication, for also gas-discharge tube lamps and photocells. Table T 10–10 A gives the composition of a photoruby glass for dark-room lamps, in which Sn and colloidal Cu are the coloring agents. The ruby color is formed by frosting with a subsequent heat-treatment (²KNAPP).

See Table T 10–2, A 4, for the composition of pale-gray neutral glasses for TV tubes, with small amounts of Ni and Co oxide additives for increasing picture contrast.

[10.2]

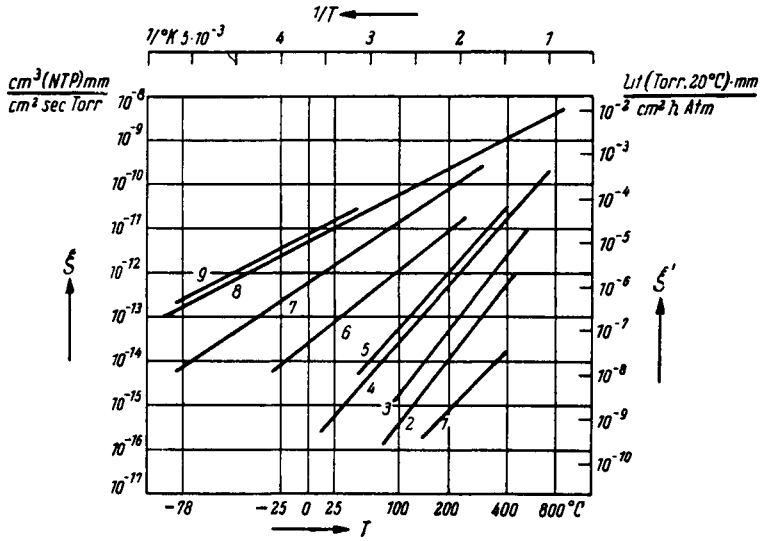


Fig. B 10-82D Permeability ξ to He (at 1 Torr gauge)(1) of glasses, as functions of temperature T (°C) and $1/T$ (1/°K) (³NORTON)(2)

CURVE	TYPE OF GLASS	MANUFACTURER	COMPOSITION (in)
1	Lead borate glass	GEN. ELEC. Co.	Table T 10–2A
2	X-ray screen glass +61% PbO	PITTSBURGH	Table T 10–11
3	Ignition tube glass No. 1720	CORNING	Table T 10–2, A 1
4	Soda-lime glass 0080	CORNING	Table T 10–2, A 1
5	Phosphate glass	HAVERFORD	Table T 10–2A
6	Borosilicate glass No. 605	OWENS	Table T 10–2, A 3
7	Pyrex glass No. 7740	CORNING	Table T 10–2, A 1
8	Quartz glass (see Table T 11–4)	–	100% SiO_2
9	Vycor, high-quartz glass	CORNING	96% SiO_2 (see also Table T 11–2)

(1) Since the partial pressure of He in the earth's atmosphere is only 5.24×10^{-6} atm $\approx 4 \times 10^{-3}$ Torr, the amount of He which enters an evacuated glass vessel from the ordinary air is

$$m_{He} = 4 \times 10^{-3}\ \xi\ (\text{cm}^3\ \text{NTP} \cdot \text{mm/cm}^2 \cdot \text{sec}).$$

(2) The parameter ξ' (right-hand ordinate) is defined as the pressure rise (Torr) per hr at 20°/cm² wall area of a glass vessel of 1 liter capacity, wall-thickness 1 mm, under a pressure gradient of 1 atm He.

So-called Luminophor glasses are produced by adding phosphors (see 15.4.V); these glasses are used for making gas-discharge lamps.

Besides colorless and tinted clear glass, there are also so-called clouded, opal or milk glasses (not to be confused with frosted glass, see 10.4.XVIII) which have achieved great importance in vacuum technology (cf. WEIGEL, HAMPTON, ¹VOLF). They contain sodium and calcium fluorides which precipitate out in the devitrification range as very

small ($<1\,\mu$) refracting particles. Gas-phase fluoride compounds also are able to play a part in this; they are homogeneously divided in the mass of the rest of the glass and

[10.2]

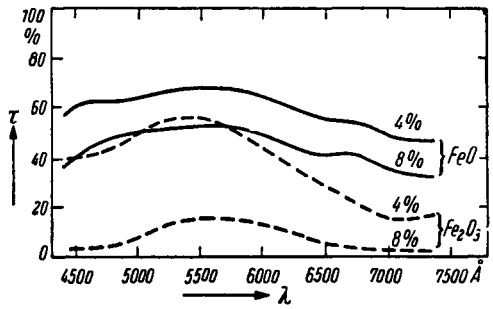


Fig. B 10-82E Transmissivity τ in the visible spectrum of glasses containing iron, as a function of wavelength λ (FRITZ-SCHMIDT)

---- 82% (SiO_2 + Fe_2O_3) + 18% Na_2O;
—— 82% (SiO_2 + FeO) + 18% Na_2O

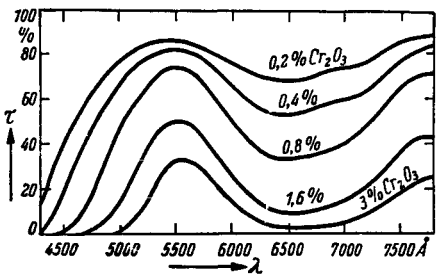


Fig. B 10-82F Transmissivity τ in the visible spectrum of glasses colored by various Cr_2O_3 contents as functions of wavelength λ (FRITZ-SCHMIDT)

Composition: 82% (SiO_2 + Cr_2O_3) + 18% Na_2O

so produce opacity. The clouding agent most used in the glass industry is cryolite (see also [1]VOLF for others); this is a naturally occurring sodium-aluminium fluoride (Na_3AlF_6). Opal glasses are more brittle than ordinary glass; they are therefore usually made as a

TABLE T 10–10. THE CHIEF OXIDES USED TO COLOR GLASS (FRITZ-SCHMIDT)

OXIDE (w/o) OF	GLASS TINT	NOTES
Cadmium (0.5% CdO + 0.02% S)	Pale yellow	For car lamp bulbs(1)
Cerium (CeO_2)	From 8%, yellow	Strong UV absorption
Iron (Fe_2O_3)	Yellow-green	Strong UV absorption
Iron (FeO)	Blue green	Strong IR absorption
Chromium (Cr_2O_3)	Intense yellow-green to green, as low as 0.2–0.4%	Strong UV absorption but good IR transmission
— (7% Cr_2O_3 + 1.3% CuO)	Green	(1)
Cobalt (CoO)	Dark blue	Good UV transmission
— (1.6% CoO + 0.2% Mn_2O_3)	Blue	(1)
Copper (CuO)	Blue	
— (2% CuO + 0.2% CoO + 0.2% Cr_2O_3)	Daylight	(1)
Manganese (2% Mn_2O_3)	Red and violet-blue	
— (16% Mn_2O_3 + 6% Fe_2O_3)	Orange	(1)
— (8% Mn_2O_3 + 3% Fe_2O_3)	Yellow	(1)
Nickel (NiO)	Reddish	
Uranium (U_3O_8)	Yellow tinge	Fluorescent; strong UV absorption
Titanium (TiO_2)	Golden yellow	
Vanadium (V_2O_5)	0.5–1%, none; 5% bright green	Strong UV absorption

(1) From [2]KNAPP.

double layer with an inner coating of ordinary glass. Table T 10–10B contains the composition of some commercial opal glasses.

Infrared transmission of technical glasses. Glass is very transparent even to heat radiation. Figures B 10-83 and B 10-84 show the transmission of a few typical glasses in the IR range (without taking reflexion into account). The IR transparency depends

TABLE T 10–10A. COMPOSITION OF PHOTORUBY BULB GLASS FOR DARK-ROOM LAMPS ([2]KNAPP)

SiO_2	PbO	Na_2O	K_2O	CuO	Sn
56.1	32.1	3.9	7.9	0.24	0.7

[10.2]

very much on the FeO content (e.g. Fig. B 10-85), less on the Fe_2O_3 content. For example, most glasses if FeO-free, pass 60% of thermal radiation when 7 mm thick, while the value for the same glass with 1% FeO is only 0.75%. Good IR absorbers are made ([2]BERGER) by introducing FeO into phosphate glasses (see Table T 10–2A), without any visible tinting effect. With the exception of B_2O_3 glasses, all untinted glass has

TABLE T 10–10B. COMPOSITION OF A FEW OPAL BULB GLASSES ([2]KNAPP)

SiO_2	B_2O_3	Al_2O_3	Na_2O	K_2O	CaO	ZnO	F
63.6	1.2	2.9	8.8	3.4	5.9	8.5	5.6
61.8	–	3.9	11,7	1.5	5.7	8.1	7.3

See also Table T 10–2, D8 (Osram opal glass 140) and Table T 10–2, D15 (Opal glass).

about the same IR transmission spectrum, i.e. high transmission up to about 2.6 μ, average transmission to 4 μ, falling to very low values at 5 μ. Ordinary Fe-free glass is therefore quite suitable for IR-sensitive photocells.[45] In the case of B_2O_3 glasses, the bands are so strongly marked above 2.8 μ that high boric oxide glass has only very low transparency above 3.5 μ (see Fig. B 10-86, curve I).

Since, in the ordinary way, an incandescent body emits a very small part of its energy as visible light and mostly as heat, knowledge of the thermal radiation transmissivity of a glass is very important for vacuum tube construction (hot-filament lamps, transmitter tubes); this is because absorption of a radiated wavelength or range of wavelengths produces heat in the glass which may bring it to softening point.[46] It can happen, for example, in transmitter tubes with plate-operating temperatures of 500 to

[45] For evacuated thermocouples used for laboratory measurements of low-intensity radiation, considering a 2 mm window thickness and 10% allowed drop in intensity, the IR limit can be shifted still further out by the following window materials: quartz to 4 μ, fluorite to 9 μ, rock-salt to 17 μ, sylvite to 21 μ. The two last have to be protected from moisture by drying agents.

[46] Bulbs for hot-filament lamps are made of soda-lime glass up to average running temperatures of 250°, in no case should the peak temperature exceed 370°. Obviously this upper limit is raised considerably by using harder glass: e.g. Vycor (95% SiO_2) will raise it to almost 800° (cf. e.g. Table T 10–4, A1). In the case of commercial radio tubes with soda-lime envelopes, the usual maximum is only 220–260°. The limit set by many manufacturers of HV tubes is even lower, generally 160°, peaks up to 220°. The limit for reliable miniature receiver tubes is not above 175° for the glass wall, or if borosilicate glass is used, not above 260°.

700° that a hard-glass envelope, even with a viscosity curve 70° higher than a soft, cannot be run any higher than a soft glass envelope of the same size and thickness because its thermal transparency is much lower than that of the soft glass. A case of

[10.2]

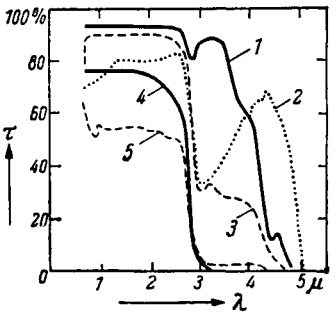


Fig. B 10-83 Transmissivity τ in the IR of quartz and binary glasses as functions of wavelength λ (FLORENCE)

1 quartz 2.9 mm thick; *2* lead-silicate glass 2.8 mm; *3* lithium-silicate glass 5.7 mm; *4* sodium-silicate glass 4.7 mm; *5* potassium-silicate glass 4.5 mm

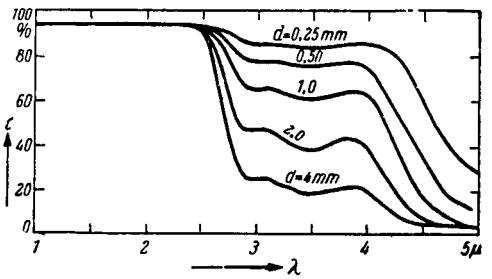


Fig. B 10-84 IR transmissivity τ of mirror glass of various thicknesses d, as a function of wavelength λ (FRITZ-SCHMIDT)

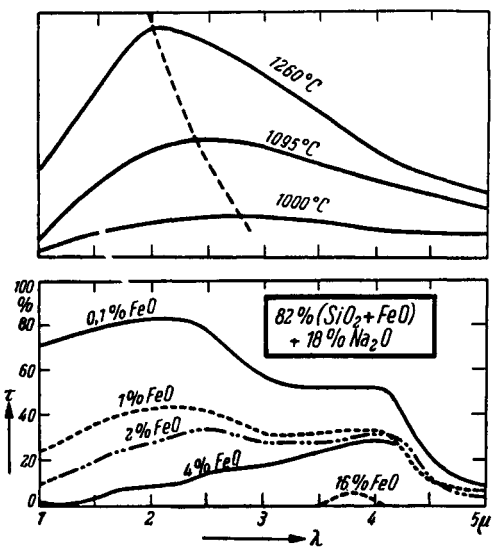


Fig. B 10-85 Transmissivity τ in the IR of glasses of composition 82% (SiO_2 + FeO) + 18% Na_2O with various FeO contents; plotted as a function of wavelength λ. Glasses fused in Pt crucibles under reducing conditions (FRITZ-SCHMIDT)

Upper curve: normalized spectral energy distribution of radiation from a black-body for three temperatures. Dashed curve: plot of the wavelength for energy maximum $\lambda_{E\,max}$.

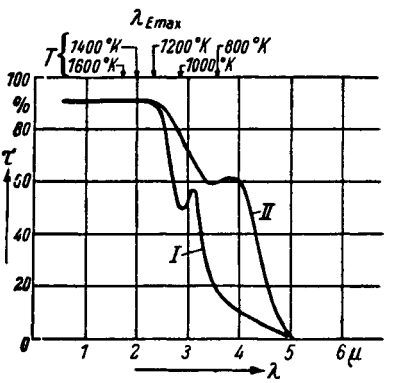


Fig. B 10-86 Transmissivity τ (for thermal radiation) of a borosilicate hard glass (I) and a soda-lime soft glass (II) of the same thickness (1 mm) as functions of wavelength λ ([1]DOUGLAS)

The upper part of the Figure shows the wavelength $\lambda_{E\,max}$ (value at which energy is maximum) for various temperatures T of the radiator

this type is shown in Fig. B 10-86. The hard-glass envelope because of its higher absorption can become about 70° hotter than the soft, and this can offset completely or more than offset its advantage in higher softening point.

The type of radiation (wavelength) that is involved can be determined from the temperature of the radiating electrode, which is easily found by a pyrometer. The black-body radiation law is then invoked. It is well known that the peak of a λ-range emitted by a hot body, the wavelength of maximum energy $\lambda_{E\,max}$, is shifted towards the shorter wavelengths as T rises, that is, into the region of higher IR transmission of glass (see upper part of Figs.B 10-85 and B 10-86). This means that the transmissivity [10.2] of a given glass rises markedly with temperature of the radiator, which is shown by the curves in Fig. B 10-87 for two CORNING glasses of different thickness. In the case of

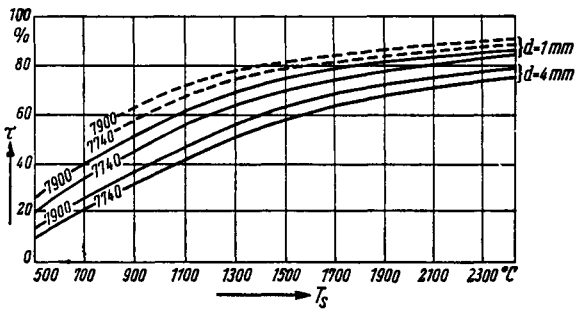


Fig. B 10-87 Transmissivity τ of two Corning glasses of different thickness d as functions of the black-body temperature of the radiator, T_s ([1]CORNING)
——— black-body source; - - - - - heated W ribbon; see Table T 10-2, A 1 for compositions of the glasses

higher temperature sources therefore (e.g. W filaments at above 2000°), most of the energy is passed through the glass by radiation, not by thermal conduction.

UV transparency of glasses. The well-known UV transparency of quartz (UV limit 1200–1800 Å) is not matched by any silicate glass, but there are many glass-forming oxides which produce glasses quite transparent to UV. For biological lamps and luminous tubes, the range 3200 to 2800 is of special interest. To this group belong the alkalis, the alkaline earths, ZnO, B_2O_3 and Al_2O_3, which have only small influence on the UV transparency limit. Clear, UV-transparent glasses can be made from them, transparent that is from the ordinary glass technologist's viewpoint. Examples are OSRAM Uviol glasses (Fig. B 10-89), CORNING UV glasses 9700 and 9741, and the well-known Vita glass (Fig. B 10-95). They are mostly used to make hard glass, but there are also soft sodium-silicate glasses with *ca.* 15% alkali oxide which have very good UV transmission down to 2500 Å ([4]STANWORTH), provided they are free of oxides of Fe, Ti, I, Cr, V, Pb, Sb and Ce. Figure B 10-88 shows a few transmission curves for UV-transparent CORNING glasses compared with Pyrex 7740 and standard window-glass (curve 10). Fig. B 10-89 (cf. also Fig. B 11-8) gives transmission curves for a series of German glasses. The UV limit is very sensitive to the ferric oxide content in particular, and rather more than to the ferrous (cf. Fig. B 10-90), but the latter gradually converts to ferric (FeO to Fe_2O_3) under prolonged UV radiation. Even 0.1% Fe_2O_3 raises the thresh-

[10.2]

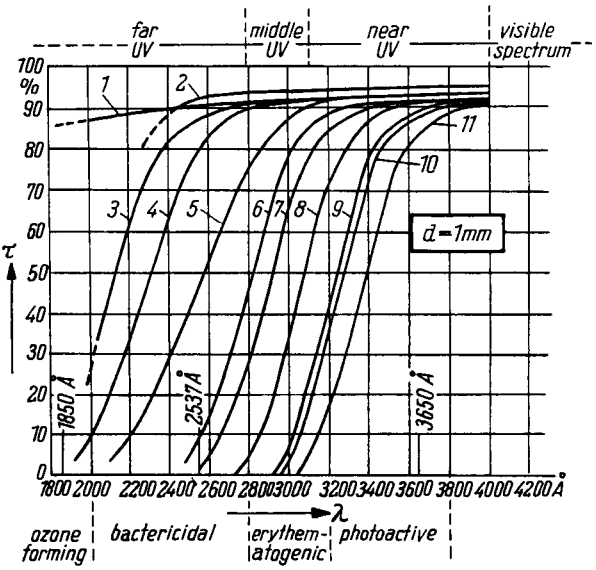


Fig. B 10-88 Transmissivity τ of Corning glasses to UV, for 1 mm thickness, as functions of wavelength λ. Pyrex 7740, Nonex 7720, lead and soda-lime glasses are shown for comparison (WEITZ)

GLASS	CURVE No.	GLASS	CURVE No.
Corex D	7	Corning 9741	4
Corning 7720 (Nonex)	11	Lead glass	9
Corning 7740 (Pyrex)	8	Lime glass	10
Corning 7912	3		
Corning 9700	6	Quartz glass	2
Corning 9720	5	Quartz crystal	1

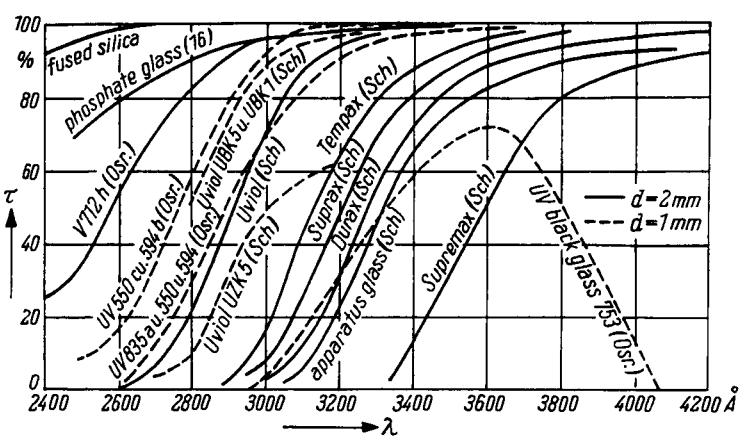


Fig. B 10-89 Transmissivity τ of different German glasses in comparison with a few standard apparatus glasses (Tempax to Supremax) and a so-called "UV black glass"; τ as a function of wavelength λ (IG = I.G. FARBEN, Osr = OSRAM, Sch = SCHOTT UND GEN.) (see also KOPEC)

old for UV from 2150–2200 to 2550 Å if the glass is 0.15 mm thick, or to 2950 Å for 1 mm (see Fig. B 10-90). Bulb glasses with good long-wave UV transmission must have an Fe_2O_3 content below 0.006% ([2]KNAPP). The Pb content also shifts the threshold to longer wavelengths; 2% PbO will raise it from 2200 to 2700 Å (see Fig. B 10-91). Above this percentage, the rise in threshold is only slow as further PbO is added. Phosphate glasses also show very high UV transmission; examples are Corex (see Fig. B 10-92, analysis in Table T 10–2, A 1) and the I.G. phosphate glass (Fig.B 10-89 and ENDE, analysis in Table T 10–2 A). If Co or Ni oxides are added to such phosphate [10.2]

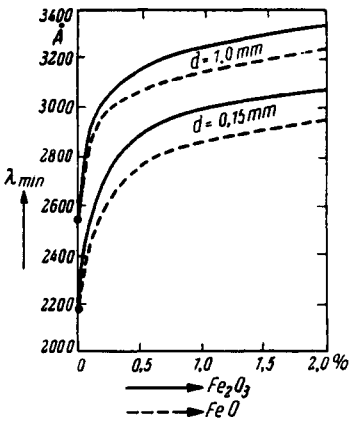


Fig. B 10-90 UV transmission threshold λ_{min} for glasses of thickness d as a function of Fe_2O_3 and FeO content

——— 82% (SiO_2 + ferric oxide Fe_2O_3) + 18% Na_2O;
- - - - 82% (SiO_2 + ferrous oxide FeO) + 18% Na_2O

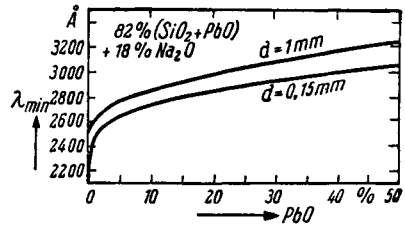


Fig. B 10-91 UV threshold λ_{min} of lead glass (82% (SiO_2 + PbO) + 18% Na_2O) as a function of PbO content (FRITZ-SCHMIDT)

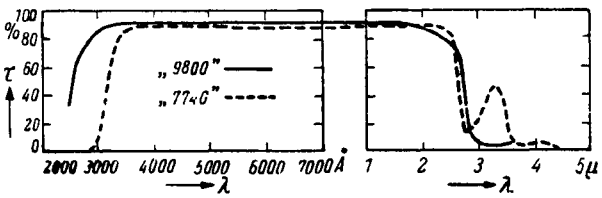


Fig. B 10-92 Transmissivity τ of two Corning glasses over the UV-IR spectrum as a function of wavelength λ ([1]CORNING)
glass 9800 : phosphate glass, clear Corex A, 1.75 mm thick; glass 7740 : Pyrex, 2 mm thick

glasses, a so-called "black" glass is produced, which transmits UV but absorbs the visible (see, e.g., OSRAM black glass 753 in Fig. B 10-89 and the black glasses of HOOLEY (see, e.g., Table T 10–2 A), which have 70% transparency even at 1 mm thickness). Pure B_2O_3 glass has very high UV transmission (λ_{min} = *ca.* 1850 Å), which is more or less impaired by addition of basic oxides (see [4]STANWORTH). Ordinary glass strongly absorbs UV (see, e.g., Fig. B 10-93 which gives the thickness dependence of the UV threshold λ_{min} of an ordinary mirror glass). At 1 mm thickness, the threshold of this glass is 2900 Å while the value for standard OSRAM lead glass (30% PbO) is 2950, and for Thüringer glass 3000 Å (LOEBE).

If UV transparent glass is exposed to intense UV for prolonged periods as in the case of the walls of UV Hg-lamps, the transmission is reduced by "solarization" so-called because sunlight produces the same effect (see, e.g., Figs. B 10-94 and 10-95). This is usually ascribed to oxidation of traces of FeO to Fe_2O_3 (NORDBERG, [2]WEYL, WHITE), and depends strongly on the composition of the glass. In many cases the original transmission can be regained by heat-treatment. The solarization effect spreads throughout

the volume of the glass, and it must be distinguished from the gradual fall-off of UV transmission caused by direct effect of the ions of Hg from the discharge, in which case a dark purely *surface* layer appears on the inner wall. Tests on Vycor glass 7910 have shown that the latter effect after 2000 hr can lead to a loss of 13% of the original transmission measured at 2537 Å.

[10.2]

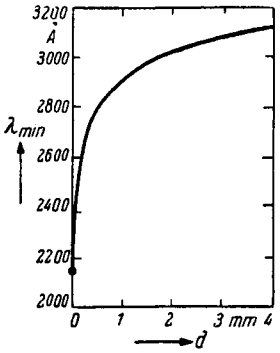


Fig. B 10-93 UV threshold λ_{min} of mirror glass as a function of thickness d, measured with UV hot-filament lamp and Hg-lamp (FRITZ-SCHMIDT)

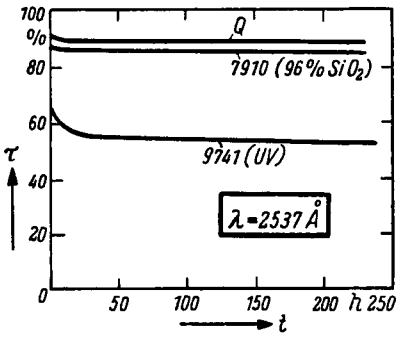


Fig. B 10-94 On the solarization effect: transmissivity τ (for $\lambda = 2537$ Å) of quartz glass (Q) and of two Corning glasses, as functions of time of exposure t while the test glass was exposed to UV from a quartz lamp at 15 cm distance (NORDBERG)

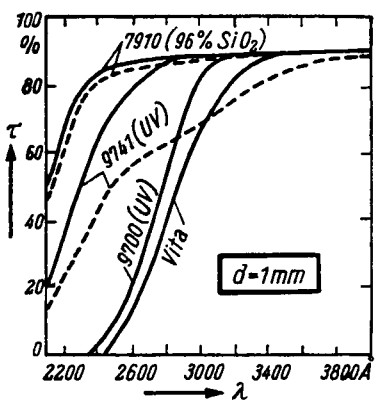


Fig. B 10-95 Transmissivity τ in the UV of some Corning UV-glasses and of CHANCE BROS. Vita glass as supplied and after solarization (curves ——— and - - - - - respectively); plotted as functions of wavelength λ (NORDBERG)

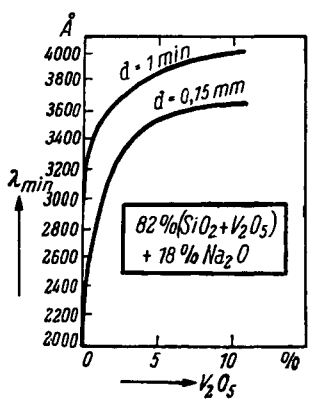


Fig. B 10-96 UV transmission threshold λ_{min} of glasses of composition 82% (SiO_2 + V_2O_5), + 18% NaO as functions of V_2O_5 content for two wall-thicknesses d (FRITZ-SCHMIDT)

UV absorbers (glasses) can be made in a wide variety of ways (see, e.g., FRITZ-SCHMIDT for further details). If the glass is to be virtually colorless, additions of oxides of V, Ce, Ti, Pb and Sb are made. UV absorbers containing TiO_2 have a very good IR transmission (up to 4 μ) but must be melted under conditions as oxidizing as possible

since otherwise reduction clouding readily occurs. Vanadium oxide is the most effective of these oxides (see Fig. B 10-96) and very small amounts will do. The effectiveness of the other oxides drops off in the order given down to the almost equal oxides of lead and antimony. Colored UV-absorbing glass of the same quality can be made by adding the various coloring oxides; no order of merit can be given.

10.2.XVII. *Transmission of X-rays and Gammas by Glasses*

The mass absorption coefficient of a glass is μ/ϱ, where μ is the absorption coefficient in cm^{-1} and ϱ is the density in g/cm^3; it can be calculated for a composite glass from the [10.2] coefficients of the individual components by linear summation. If m_i is the weight fraction of the ith component, then for n components we have:

$$(\mu/\varrho)_{\text{glass}} = \sum_i^n m_i (\mu/\varrho)_i .$$

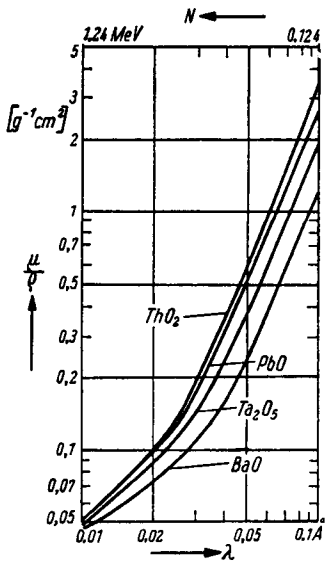


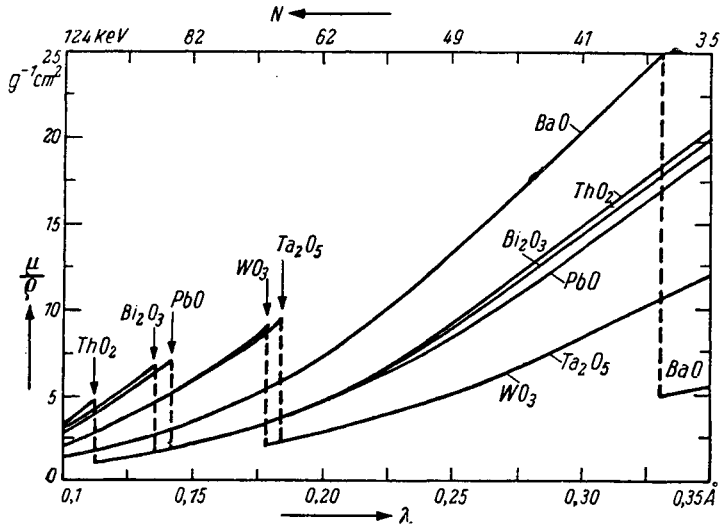
Fig. B 10-97 (part I) Mass absorption coefficient μ/ϱ for X- and gamma-radiation of glass-forming oxides, as functions of wavelength λ and energy in MeV (N)
I range 0.01–0.1 Å and 1,240,000 to 124,000 eV.
(II — IV see page 142)

The absorption coefficient of the glass can then be found by multiplying the mass coefficient by the glass density. The mass coefficients of the chief glass-forming oxides are given in Fig. B 10-97, I—IV, as functions of λ (Å) and energy N (eV) for the range 0.01 Å to 0.1; 1,240,000 eV to 124,000. For higher energies (gammas), most of the data are lacking but one can use as a guide the fact that the absorption coefficient above 1.2 MeV energy begins to rise again due to "pair formation" and that the mass coefficient rises with atomic number.

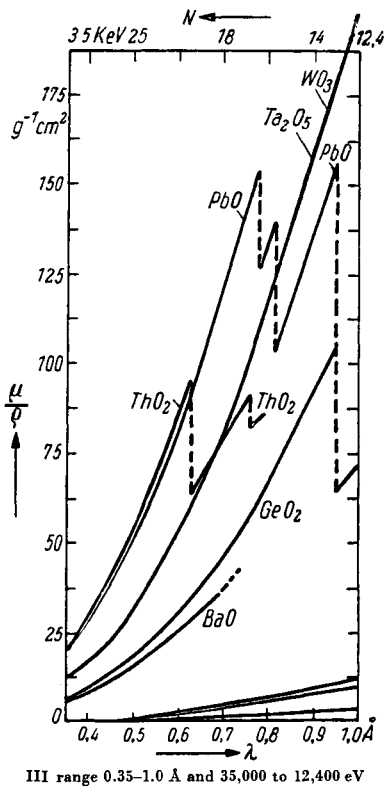
The mass coefficient curves are in agreement with the fact that for short-wave X-rays and gammas ordinary Pb-free glass is sufficiently transparent (see, e.g., the curves for Pyrex in Figs. B 5.6-2, B 5.6-3, and collection of curves in Fig. B 10-97A; see also SEREN for gamma-ray windows of very thin Pyrex).

Exposure to X-rays discolors ordinary glass similarly to solarization by UV (see KERSTEN, NÜRNBERGER, ZUNICK and Fig. B 10-98). The glass often takes on a bright

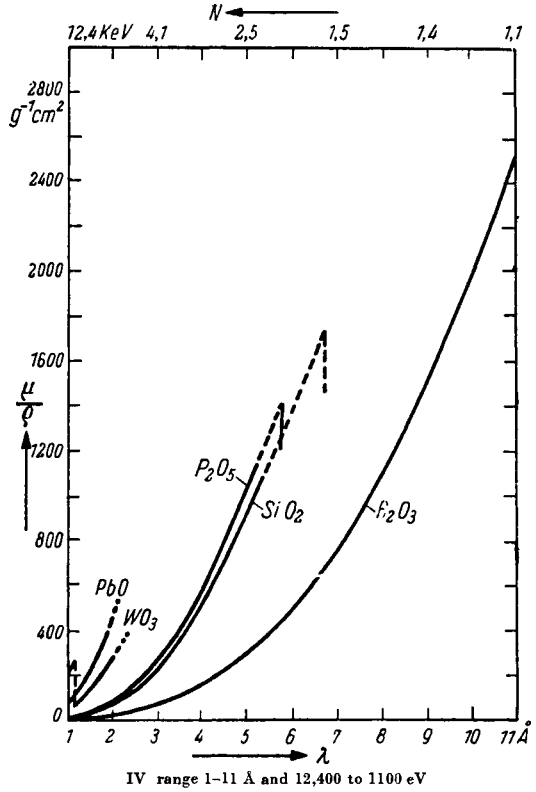
[10.2]



II range 0.1–0.35 Å and 124,000 to 35,000 eV



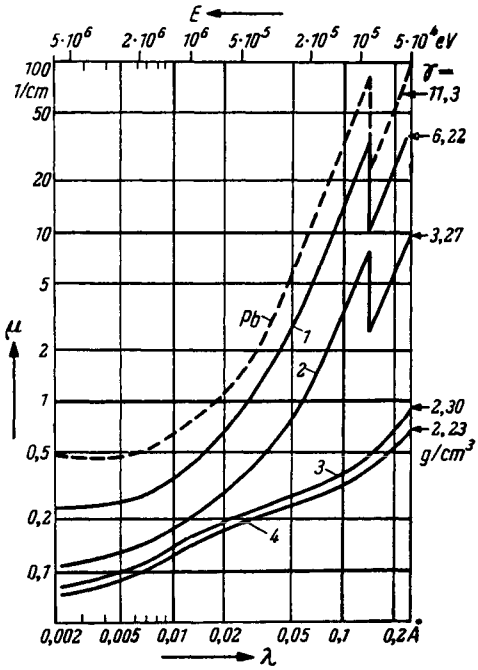
III range 0.35–1.0 Å and 35,000 to 12,400 eV



IV range 1–11 Å and 12,400 to 1100 eV

Fig. B 10-97 Mass absorption coefficient μ/ϱ for X- and gamma-radiation of glass-forming oxides, as (part II–IV) functions of wavelength λ and energy in KeV (N)

yellow tint which changes to deep brown on long exposure. While it is true that this discoloration and the resulting drop in transmission in the visible range in X-ray tubes is generally of no technical interest,[47] it is very harmful in TV projection tubes, where



[10.2]

Fig. B 10-97A Absorption coefficient μ of various glasses for X- and gamma-radiation compared with lead (density $\gamma = 11.3$ g/cm³), as functions of wavelength λ and energy of radiation E ([3]SHAND); cf. also Fig. B 10-100A

1 high-lead Corning 8363 (76% Pb); *2* lead glass Corning 8362 (30% Pb); *3* soda-lime glass; *4* low-expansion borosilicate glass

because of high operating voltages, deceleration of the electrons incident on the fluorescent screen produces X-rays, which even after only 20–30 hours operation can lower the transmission of the glass to the fluorescent light from the picture screen to 50%.[48]

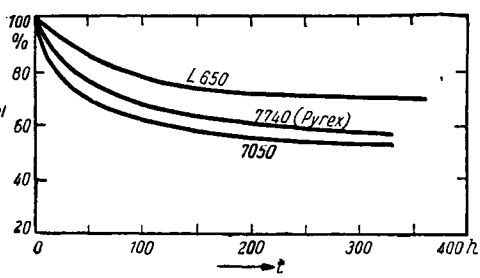


Fig. B 10-98 Fall in transmissivity to visible light of various glasses which have had prolonged exposure to the effects of X-rays (35 kV, Cu anode, 0.75 mm Be filter) (ZUNICK)

τ_{rel} = transmission relative to initial value; t = exposure time

This effect can be much reduced by addition of Ce (0.8–2.4% CeO_2) and avoidance of light-reducing components (PbO) ([2]SMELT; see also [3]GIER and Table T 10–2, H). In these glasses which contain Ce, the transmission of visible light drops by 20–25% in a

[47] A worse effect is the electrolysis caused by fast electrons penetrating the glass; this also contributes to discoloration and to surface cracks, which themselves lead to electrical breakdown or mechanical fracture.

[48] Electrolysis plays a part here also; electrons enter the glass through the layer of phosphor and cause discoloration. See 10.2.XI for the reduction of this effect.

few hours, but then does not alter appreciably in several hundred hours. By the addition of 0.5% CeO_2 to Kovar glass of standard composition, a glass (L 605) has been made for X-ray tubes whose analysis is given in Table T 10–2, A3, and properties in Table T 10–4, A3. Its discoloration is much less than that of ordinary CORNING 7740 Pyrex and of 7050, as can be seen from Fig. B 10-98.

Glasses which must be transparent to X-rays in the longer wavelength region (soft X-rays) only employ oxide components of low molecular weight (see Fig. B 10-97), i.e.

10.2]

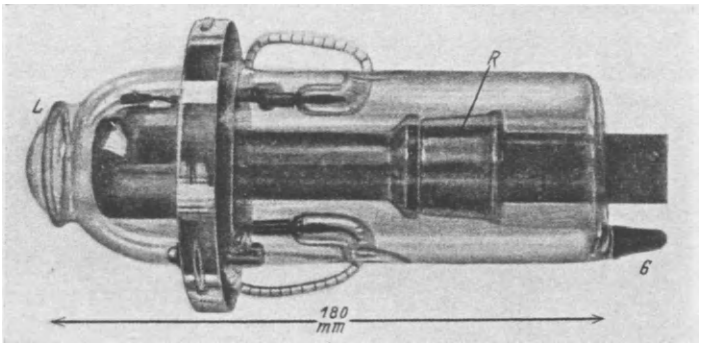


Fig. B 10-98A Grenz-ray tube with LINDEMANN glass window sealed to envelope glass (Manufacturer: SIEMENS-REINIGER-WERKE)
L Lindemann window; *R* Cu-ring joined to tube glass; *G* rubber cap to protect seal-off

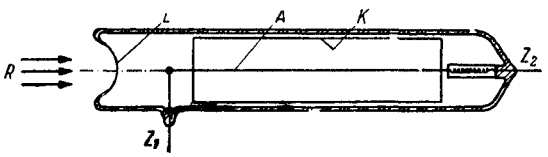
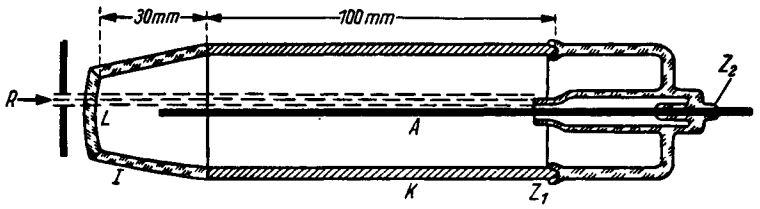


Fig. B 10-99 Diagram of X-ray counter tube construction with envelope of glass and a LINDEMANN window
A anode; *K* cathode; Z_1 and Z_2 leads sealed into glass; *L* a sealed-in window (blown concave) made of 0.1 mm thick LINDEMANN glass; *R* X-ray beam (direction of entry)

low atomic number; e.g. oxides of B, Li and Be. A glass of this type is the well-known LINDEMANN glass (see Tables T 10–2A, T 10–4B). Its absorption and transmission coefficients behave as shown in Figs. B 5.6-3 and B 5.6-4. According to BLEEKSMA, the transmission is still 75% through a LINDEMANN glass 250 μ thick for K_α radiation from a Cu anode ($\lambda \approx 1.5$ Å), and according to BRACKNEY it is 60–65%. This glass can be joined to Thüringer apparatus glass and Pt-sealing glass, as in the form of a round window (see Fig. B 10-94A). However, it is not resistant to weathering, and has to be protected from the atmosphere by a special lacquer (e.g. Herbal varnish). In the manufacture of X-ray counter tubes, similar to Geiger counters, LINDEMANN glass is used in 0.1–0.25 mm thickness windows with convex or concave curvature (see Figs. B 10-99, 10-99A, Fig. B 4.1-8 and BLEEKSMA, FRIEDMAN).

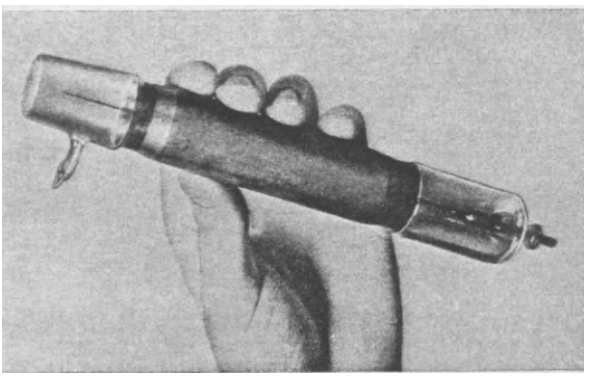
If it is desired to produce X-ray shield glass with high absorptivity for X-rays, oxides with the highest possible atomic weight must be used (Fig. B 10-97). The chief com-

ponent of these ordinary, clear silicate glasses is PbO (see Fig. B 10-100). The main addition to the melt is BaO because of its relatively high molecular weight. The com-



I

[10.2]



II

Fig. B 10-99A X-ray counter tube (BLEEKSMA) with cathode cylinder of CrFe (30/70) and intermediate glass section *I* of ordinary soft glass ($\alpha = 95 \times 10^{-7}$ l/°C) for reliable joint to convex 0.25 mm thick LINDEMANN glass window *L*; other dimensions as in Fig. B 10-99; gas-filling of the counter to measure K_α radiation from Cu or Fe: argon at 300 Torr + traces of organic quenching agent (vapor)

I schematic; II production model (courtesy of PHILIPS). For Geiger-Müller counters see 20.7.III

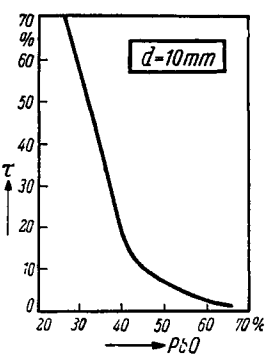


Fig. B 10-100 X-ray transmission τ (100 kV, W anode source) of 10 mm thick shield glass, as a function of lead content (PbO)

position, density and lead equivalent thickness of these highly transparent silicate glasses are given in Table T 10–11. (The lead equivalent is the ratio of the absorption coefficients of the X-ray shielding glass and that of lead for the same energy of radia-

TABLE T 10-11. COMPOSITION AND CHIEF PROPERTIES OF SOME X-RAY SHIELDING GLASSES

SILICATE GLASS	COMPOSITION (w/o)						DENSITY	Pb EQUIV. (100 KeV)	T_{soft}[1]	DIS-COLOR-ATION [2]	H_2O ATTACK (VAPOR)[3] TIME	AUTHOR
	SiO_2	PbO	BaO	Na_2O	OTHER		(g/cm³)	(%)	(°C)		(hr)	
Lead silicate 40	x	40		x			3.35	12				UNGELENK
Lead silicate 51	x	51		x			3.81	18				UNGELENK
Lead silicate 65	x	65		x			4.56	23–30				UNGELENK
X-ray shield, clear 687							2.70	5.4[5]				OSRAM
X-ray shield, clear 187							3.20	9.5[5]				OSRAM
X-ray shield, clear 711 a							3.60	15.4[5]				OSRAM
X-ray shield, clear 535 a							3.88	18.2[5]				OSRAM
X-ray shield, clear 646 a							4.45	23.2[5]				OSRAM
X-ray shield, opal 660 g							3.87	17.6[5]				OSRAM
X-ray shield, black 689 a							4.56	24.4[5]				OSRAM
Mervin No. 19	15.2	82.6	—	2.3			6.367	≈47			Not stable	MOREY
Russian glass	36	51		6.9	CaO :3.5							[2]KNAPP
PP glass[4]	29	62	8.5	—			4.941	32.5	625	Deep red brown	100	ROTHERMEL
PP glass[4]	31	61	8									[3]NORTON
PHOSPHATE GLASS	P_2O_3	PbO	WO_3	TiO_2	CdO	ThO_2						
Auer glass	31	42.6				13						[2]KNAPP
Glass No. 260[6]	16.1	60.0	21.3	1.0	1.6	—	6.583	57.8	480	Not visible	25	ROTHERMEL
Glass No. 266	16.4	58.6	21.7	2.5	0.8	—		55.2	480	Not visible	80	ROTHERMEL

(1) $\eta = 10^{7.6}$ P (see Table T 10–5).
(2) After 1.5 hr exposure to 200 kV radiation at 50 mm from anode (W).
(3) Time taken for 1 atm water vapor to produce visible surface attack on glass.
(4) Commercial product of the PITTSBURGH PLATE GLASS CO. (see also Fig. B 10-100A).
(5) For 180 kV X-ray tube voltage. (6) See also Fig. B 10-100A.

tion, i.e. $\mu_{(glass)}/\mu_{Pb}$.) Other oxides, those of Bi, Th, U, Ta and W, may also be added (see, e.g., Fig. B 10-97, GOTT, SINGER, [2]SUN).

It is unfortunate that high-lead silicate glasses are not chemically inert, and when exposed to energetic X-radiation for 10–15 minutes, exhibit marked discoloration. Lead borate glasses, of course, are colored dark orange and are not in question for this purpose. There has been a recent success in the production of high-lead phosphate

[10.2]

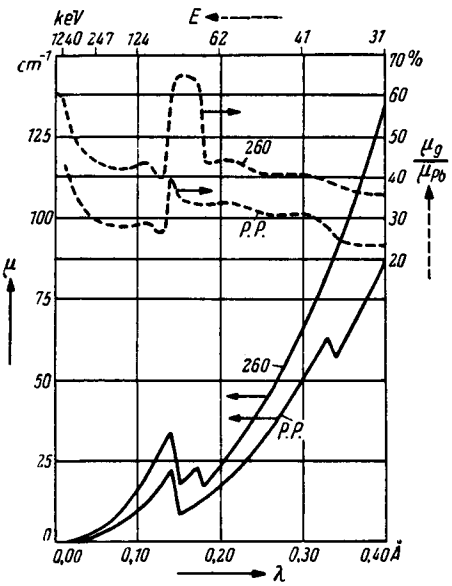


Fig. B 10-100A Absorption coefficient μ for X-rays (———) and lead equivalent (μ_g/μ_{Pb}) (– – –) of a phosphate X-ray shielding glass "No. 260" and a commercial lead-barium silicate glass "P.P.", as functions of wavelength λ and energy E of the absorbed radiation (ROTHERMEL)
Composition of both glasses given in Table T10–11

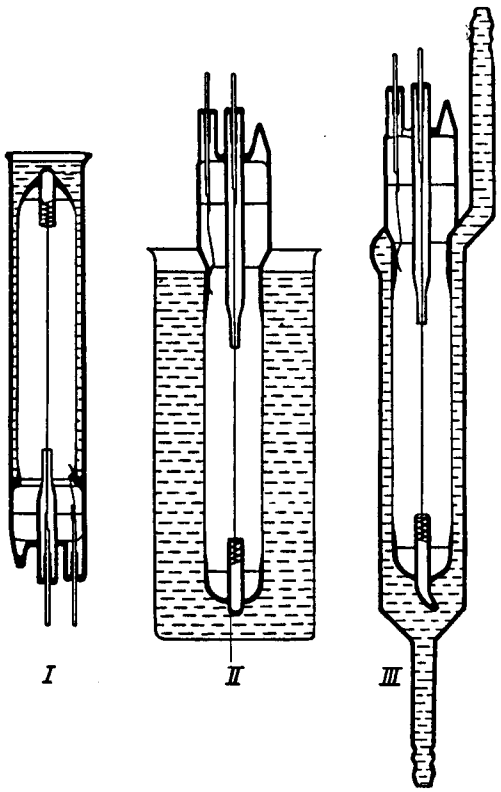


Fig. B 10-100B Construction of Geiger-Müller counters made from 0.1 mm wall glass tube, for determination of activity of liquids (BÖHM)
I beaker type; II immersion type; III flow type (cf. also Fig. B 7.8-1)

glasses based on the complex $PbO—WO_3—P_2O_5$ with small additions of TiO_2 and CdO; these have been made at relatively low temperatures, they are resistant to atmospheric weathering, have low tendency to devitrification and show no discoloration when exposed to hard X-ray or gamma-radiation (ROTHERMEL). Because of their high solubility for PbO and WO_3, they have a large content of heavy oxides and their lead equivalent thickness is higher than that of the best commercial lead silicate X-ray shielding glasses (see Table T 10–11 and Fig. B 10-100A).

10.2.XVIII. *Beta Transmission*

(BÖHM)

Since the β-transparency of any material depends only on the mass density $\varrho \cdot d$ (density $\times$ thickness) (see also Fig. B 13-13), Geiger liquid counters (Fig. B 10-100B) are made of a strong glass with a wall-thickness of only about 0.1 mm, the mass density is only about 20–50 mg/cm^2. 75% betas from radioactive P^{32} (max. beta energy 1.69 MeV) can penetrate the glass walls (cf. also Fig. B 13-13).

[10.2]

10.2.XIX. *Transparency of Glasses to Neutrons*

([3]SUN, U.S. GOVERNMENT)

With the development of nuclear physics came the question of the transmission of neutrons through glasses, mainly the result of a need for special neutron-absorbing glass shields. Table T 10–12 contains the essential absorption data for the oxides of primary importance in glass manufacture, arranged in alphabetical order, for the case of neutrons of thermal energy (0.025 eV). Since Cd metal plays the same part in neutron absorption that Pb does for absorption of X-rays and gammas, columns 5 and 6 of Table T 10–12 contain values of the ratio μ_{Cd}/μ_x (where these parameters are respectively absorption coefficients for Cd metal and for a hypothetical glass made from the oxide x), and also the inverse ratio which is known as the cadmium equivalent (%). The last column (7) contains the so-called mass absorption coefficient μ/ϱ, where μ is the ab-

TABLE T 10–12. PROPERTIES OF GLASS-FORMING OXIDES: ABSORPTION OF THERMAL NEUTRONS (0.025 eV) (see [3]SUN)

OXIDE x	DENSITY ϱ_x (g/cm^3)	ABSORPTION COEFF. μ_x (cm^{-1})	HALF-THICKNESS[1] $(t_{1/2})_x$ (cm)	RATIO[2] μ_{Cd}/μ_x	Cd EQUIVALENT[2] μ_x/μ_{Cd} (%)	MASS ABSORPTION COEFF. μ_x/ϱ_x (cm^2 g^{-1})
Al_2O_3	3.8	0.355	1.95	307	0.326	0.0935
B_2O_3 glassy	*1.81*	*22.8*	*0.0304*	*4.77*	*21*	*12.6*
BeO	3.00	0.546	1.27	199	0.5	0.182
CdO	*8.15*	*90.0*	*0.0077*	*1.21*	*82.7*	*11.0*
Eu_2O_3	*7.42*	*116.9*	*0.0065*	*0.93*	*107.5*	*15.8*
Gd_2O_3	*7.41*	*1130*	*0.00061*	*0.096*	*1040*	*153*
FeO	5.75	0.843	0.822	129	0.775	0.147
Fe_2O_3	5.20	0.769	0.902	142	0.704	0.148
In_2O_3	*7.04*	*5.98*	*0.116*	*18.2*	*55*	*0.853*
Li_2O	*2.01*	*5.99*	*0.116*	*18.2*	*55*	*2.99*
MgO	3.58	0.385	1.80	283	0.35	0.108
P_2O_5 glassy	2.74	0.348	1.99	313	0.32	0.127
PbO	9.49	0.328	2.11	332	0.31	0.0346
Sb_2O_3	7.86	0.551	1.26	198	0.505	0.070
SiO_2	2.20	0.238	2.91	457	0.219	0.108
SnO	6.25	0.243	2.85	448	0.223	0.037
WO_3	7.16	0.662	1.05	164	0.61	0.0926
ZnO	5.66	0.356	1.94	306	0.327	0.0629

[1] $(t_{1/2})_x = 0.693/\mu_x$.

[2] μ_{Cd} (for 0.025 eV neutrons) = 108.9 cm^{-1}.

sorption coefficient and ϱ is the density (g/cm^3). This parameter is not dependent on the physical state of the oxide and it can be calculated for an n-component glass by the expression:

$$(\mu/\varrho)_{\text{glass}} = \sum_{i=1}^{n} m_i \, (\mu/\varrho)_{\text{oxide } i},$$

where m_i is the weight fraction of the ith component, i.e. $\sum_{i=1}^{n} m_i = 1$. Table T 10–12 shows plainly that, of the usual, cheap, glass-forming oxides for strong neutron-absorbers, CdO and B_2O_3 are the chief ones, that of the rare oxides the chief ones are [10.2]

TABLE T 10–13. NEUTRON ABSORPTION PROPERTIES OF A SPECIAL GLASS ABSORBER (33% B_2O_3, 55% CdO, 12% In_2O_3) FOR VARIOUS NEUTRON ENERGIES E_N (3SUN)

E_N (eV)	ABSORPTION COEFFICIENT μ_{glass} (cm^{-1})	CADMIUM EQUIVALENT $\mu_{\text{glass}}/\mu_{\text{Cd}}$ (%)
0.025(1)	46	42(4)
1.4(2)	26	4700
10(3)	1.2	580

(1) $\mu_{\text{Cd}} = 108.9$ cm^{-1}.
(2) $\mu_{\text{Cd}} = 0.55$ cm^{-1}.
(3) $\mu_{\text{Cd}} = 0.21$ cm^{-1}.
(4) Cd equivalent for ordinary glass $\approx$ 0.1–0.2%.

Gd_2O_3 and Eu_2O_3, and that the ordinary components of silicate glasses of standard type (oxides of Si, Li, Al, Mg, Pb, Zn, Fe, etc.) have a relatively high transparency for neutrons.

Although the data in Table T 10–12 only hold for thermal neutrons, they provide in general an adequate guide to the relative absorption for neutrons of higher energy. There are, however, oxides which have a selective high absorption for neutrons of specific energies. An example is indium (In_2O_3) which has an absorption resonance that is quite sharp near 1.4 eV, a common energy for neutrons to have (see Fig. B 10-101). Indium oxide is therefore of special importance for glasses designed to absorb neutrons of this energy. Table T 10–13 gives absorption data for a cadmium-indium-borate glass; it should be noted here that the Cd equivalent at 0.025 eV of ordinary glasses (window-panes, tubes, usual X-ray screening) is only about 0.1–0.2%. For neutrons of energy 1.4 eV, this glass has the astonishing Cd equivalent of 4700% (i.e. $\mu_{\text{glass}}/\mu_{\text{Cd}} = 47$).

The high absorption of gadolinium oxide (see Fig. B 10-101) has led to the manufacture of glass of the composition 33% B_2O_3, 35% CdO and 32% Gd_2O_3, but because of the rarity and cost of Gd (like Eu), this is seldom a practical proposition.

When using the data of Table T 10–12 for making neutron-absorbing glass, one should obviously take into account that, apart from the cost of initial materials, the product has to be made by ordinary methods of glass technology, should not devitrify on cooling (crystallize) and should be resistant to weathering, because moisture-sensitive glasses in particular are of no use in practical work. The last point is involved in making borate

glasses of CdO contents between 56 and 70%, which can be easily melted (1100°) from cadmium carbonate and boric oxide. The manufacturers of neutron-absorbing glasses are therefore forced to select components on purely glass-technological grounds, and

[10.2]

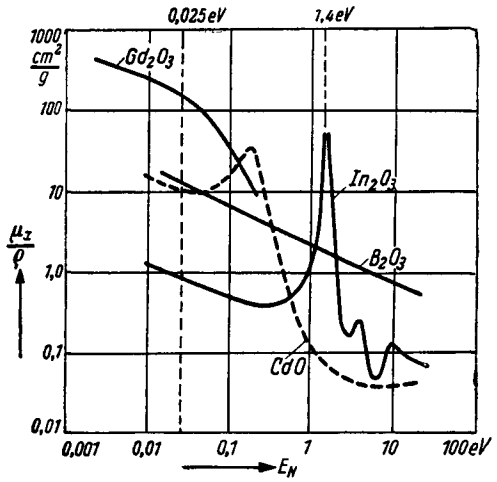


Fig. B 10-101 Mass absorption (scattering) coefficient μ_x/ϱ of some glass-forming oxides, as functions of neutron energy E_N

choose ones which may also have a low neutron absorption coefficient (e.g. SiO_2), particularly in cases where there are special demands for chemical corrosion resistance. In this connection, neutron-shielding glasses have been recently produced which are resistant to atmospheric corrosion; they are based on $CdO—SiO_2—B_2O_3$ mixtures and melted at 1250–1400°, CaF_2 being added as fluxing agent and Al_2O_3 to retard devitrification (MELNICK). Table T 10–14 gives their compositions and neutron absorption properties.

TABLE T 10–14. COMPOSITION OF WATER-VAPOR-RESISTANT GLASSES BASED ON $CdO—B_2O_3—SiO_2$, AND THEIR ABSORPTION PROPERTIES FOR THERMAL NEUTRONS (0.025 eV) COMPARED WITH ORDINARY GLASSES (MELNICK)

TYPE OF GLASS	COMPOSITION (w/o)						DENSITY	TRANSMISSION (2 mm glass)	ABSORPTION COEFFICIENT μ	Cd EQUIVALENT μ_{glass}/μ_{Cd}
	CdO	B_2O_3	SiO_2	CaF_2	Al_2O_3		(g/cm^3)	(%)	(cm^{-1})	(%)
Neutron absorption glass 1	64.3	0.0	26.1	8.5	1.1		4.632	0.139	32.9	30.2
Absorption glass 2	58.1	2.1	29.4	9.5	0.9		4.278	0.322	28.7	26.3
Absorption glass 3	55.7	11.2	19.3	12.6	1.2		4.288	0.153	32.4	29.7
	SiO_2	PbO	Al_2O_3	Na_2O	CaO	BaO				
X-ray shielding glass "PP"[2]	29	62	—	—	—	8.5	4.929	97.2	0.141	0.141
Ordinary window glass	71	—	1.5[1]	15	12	—	2.541	97.8	0.113	0.104

[1] Fe_2O_3 included.

[2] Made by PITTSBURGH PLATE GLASS CO.

10.2.XX. *Chemical Resistance of Technical Glasses*

Although vacuum technology is less exacting in its chemical requirements for glass than chemistry, bacteriology or medicine, tubes and lamps have to be used in the open air, stocks of glass may have to be stored for prolonged periods, chemical baths are used for glass cleaning, there are degassing processes to consider (see also Section 10.5), and discharge devices have vapor fillings; these facts involve, at the very least, the characteristic behavior of glass in the presence of the chief reagents. The effects of most concern are those of atmospheric moisture, alkalis, ordinary mineral acids, hydrofluoric and phosphoric acids, and certain metallic vapors like those of Hg or Na. [10.2]

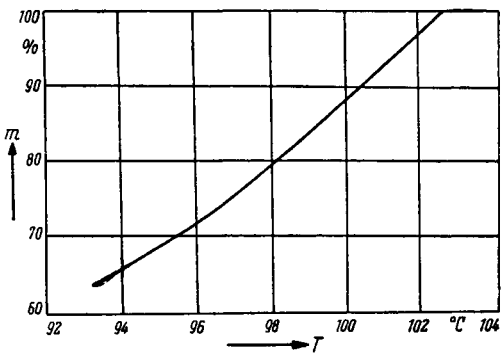


Fig. B 10-101 A Temperature-dependence of water attack on glass. The amount dissolved (m) is measured as a function of water temperature T, the amount dissolved at 102.5° being set at 100% (FRANK)

Resistance to water. The effect of H_2O and steam on glass, which generally contains alkali or alkaline earth ions, is to break up the Si—O—X bonds; X represents an alkali or alkaline earth ion (Na^+ and others like it) which forms a water-soluble salt (e.g. NaOH) and is leached out of the glass. The original Si—O—X chain converts to Si—O—H by ion exchange between Na and OH; a "hydrogen glass" thus forms on the glass surface, where the only rate-controlling step is the diffusion of surface Na ions. The hydrogen glass is a gel which has on one side the original Si—O—Si bonds and on the other Si—O—H bonds. If the solution products are washed away by the water, the Si—O—Si bonds are mainly undamaged, or any surface damage may be removed by washing with HF. However, if the hydrolysis products remain in the gel, subsequent reactions resemble the much more severe effects of alkaline solutions on glass, discussed below. CO_2 from the atmosphere then forms Na_2CO_3, which does not have any further effect on the SiO_2 in the glass. These destructive processes are accelerated by temperature, and the rate of attack is roughly doubled every 10° (see Fig. B 10-101 A–C). Superheated steam has a particularly powerful effect (see Fig. B 10-102); this arises in sterilization of glass in autoclaves, and when steam condenses above the water-line in water-level sight glasses.

The resistance of silicate glass to H_2O generally falls as the alkali content increases and rises with SiO_2 content, and to some extent with ZnO, Al_2O_3 and B_2O_3. Since the various components of a glass interact with each other, it is not always possible to draw reliable conclusions about the chemical resistance to H_2O and its vapor from the composition. Resistance to hydrolysis has to be determined experimentally by expos-

[10.2]

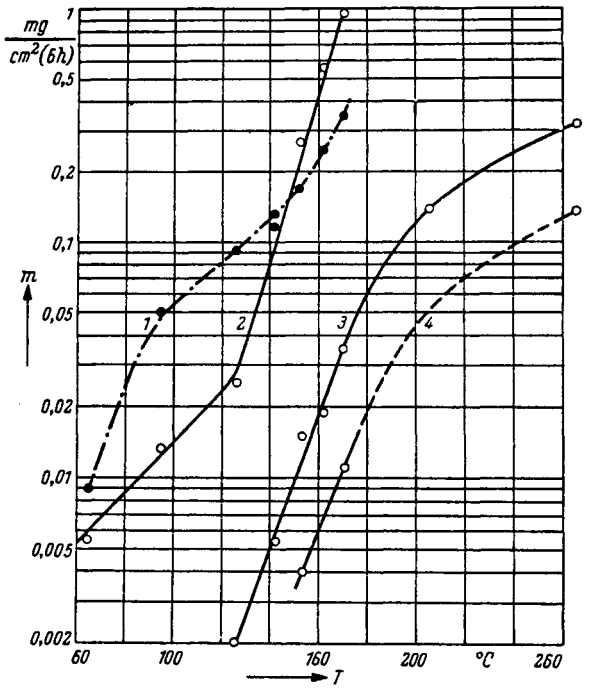


Fig. B 10-101B Attack on various glasses by distilled water (mg dissolved m/cm^2 of surface in 6 hr) as a function of temperature T (TAYLOR)

1 soda-lime glass bulbs; *2* Pb glass used in electrotechnical work; *3* borosilicate glass of low thermal expansion; *4* high-lead silicate glass with 58% PbO

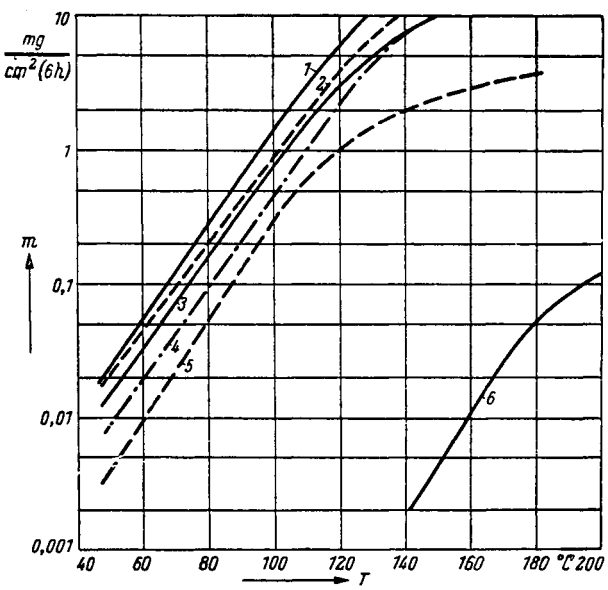


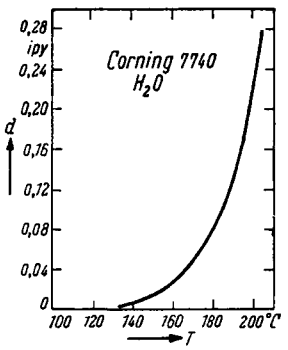
Fig. B 10-101c Temperature-dependence of attack on glass by aqueous alkali solutions measured by amount m dissolved/cm^2 of surface in 6 hr ([3]SHAND)

In *1* 5% NaOH, *2* 6.9% KOH, *3* 5% Na_2CO_3, *4* 1% NaOH — low-expansion borosilicate glass

5 5% NaOH, *6* distilled water — "alkali-resistant" glass

ing glass to water for a definite time at a definite temperature and measuring the amount of alkali that goes into solution. This process is standardized.

According to DIN 12111, 2 g of powdered glass, 0.5–0.3 mm grain size, is placed in a small vessel of very resistant glass and exposed for 1 hr to the effects of distilled water at 100°, whose alkali constant is then determined by normal titration methods



[10.2]

Fig. B 10-102 Corrosion depth d of super-heated steam in Pyrex 7740 (Corning) as a function of steam temperature T ([1]CORNING); the depth is calculated from the weight loss and is usually given in in./year (ipy)

with N/100 HCl and methyl-orange as indicator. The amount of HCl needed to change the color of the solution gives the amount of Na_2O leached from the glass and this fixes the hydrolytic classification, as in Table T 10–15. Table T 10–4 contains data of this kind for commercial glasses in sections C, D 1, D 9, D 13, D 14 and D 16 to D 25.

There is an older method used by the Deutsche Glastechnische Ges. (DGG). Glass powder of 0.5–0.3 mm sizing is obtained, equal in weight (g) to four times the density of the glass (g/cm³), i.e. 4 cm³, and is boiled for 5 hours in 100 ml of distilled water; after filtration and evaporation of the solution, the residue is weighed (mg). It comprises

TABLE T 10–15. HYDROLYTIC RESISTANCE (INERTNESS TO WATER) OF GLASSES. CLASSIFICATION FOLLOWS DIN 12 111

HYDROLYTIC CLASS	DESIGNATION (MYLIUS)	ALKALI YIELD mg Na_2O	CONSUMPTION OF ACID[1] cm³ N/100 HCl	NOTES
		for 2 g of ground glass		
I	Water-resistant	≤ 0.06	≤ 0.2	High resistance even at high temperatures, required for analytical work
II	Resistant glass	> 0.06–0.12	> 0.2–0.4	
III	The harder apparatus glasses	> 0.12–0.53	> 0.4–1.7	Adequate for most room-temp. analytical work
IV	Softer apparatus glasses	> 0.53–1.24	> 1.7–4.0	For laboratory work where components from the glass exert no harmful effects
V[2]	Defective hydrolytically	> 1.24	> 4.0	E.g.: LINDEMANN glass, and many Kovar glasses

[1] 1 cm³ 1/100 normal HCl is equivalent under these test conditions to 0.31 mg Na_2O.
[2] Not given in DIN 12111, but often required in practice.

not only the dissociated fraction (Na_2O) as in the DIN 12111, but also B_2O_3 which remains undissociated in the solution, and a colloidal suspension of SiO_2. This quantity is called the "water-solubility", or "Auslaugung" (leaching, wet-extraction) in the DGG method. Table T 10–4, C, col. 10, gives the mg value, and Table T 10–15 A the classification corresponding to the method.

TABLE T 10–15A. HYDROLYTIC CLASSIFICATION BY STANDARD TESTS ON GROUND GLASS, AS CARRIED OUT BY THE DEUTSCHE GLASTECHNISCHE GESELLSCHAFT (DGG) ([1]ANON.)

[10.2]

DGG CLASS	AMOUNT LEACHED OUT IN DGG TEST (mg)	TYPE OF GLASS
I	0–10	Water-resistant glasses
II	10–15	Resistant glasses
III	15–25	Hard apparatus glasses
IV	25–50	Soft apparatus glasses
V	over 50	Chemically inferior grades

Table T 10–15 B gives some test results on groups of glass obtained by American tests.

In contrast to these methods where the corrosive medium in contact with glass is not renewed, recently proposed test methods involve exposure of powdered glass to a stream of freshly distilled water. Further details are given by BEATTIE.

In vacuum-tube construction, hydrolytic classification helps to evaluate how a glass will behave in storage, or how a glass bulb will resist atmospheric effects (luminous tubes and lamps operating out of doors). If glass that has been attacked hydrolytically by prolonged storage in a damp place is worked in the heat of a gas-torch, wrinkles form

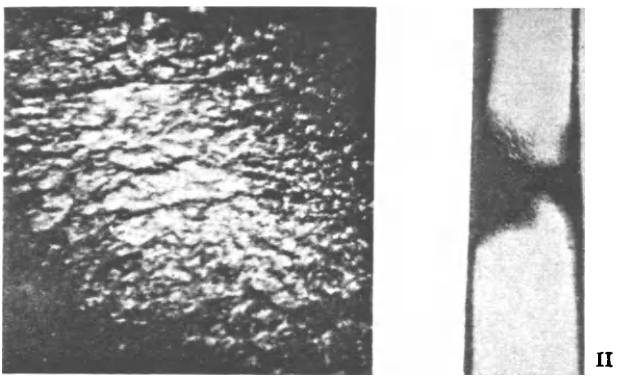
TABLE T 10–15B. HYDROLYTIC RESISTANCE OF VARIOUS GROUPS OF GLASSES ACCORDING TO AMERICAN TESTS ([3]SHAND)

TYPE OF GLASS	TEST CARRIED OUT BY	
	AMER. PHARM. SOC.[1]	ASTM-A[2]
	Na_2O YIELD (w/o)	Na_2O YIELD (w/o)
Soda-lime, plate glass	0.03	–
Soda-lime, hollow-ware	0.05	0.03
Soda-lime, lamp bulbs	0.09	0.04
Lead glass, electrical purposes	0.07	0.15
High-lead glass	0.0006	–
Alumo-borosilicate apparatus glass	–	0.005
Low expansion borosilicate (e.g. Pyrex)	0.0025	0.005
Borosilicate W glass (sealing)	0.13	–
Alumosilicate glass	0.003	0.06
Alkali-resistant glass	–	0.05
Vycor glass (96% SiO_2)	0,0003	0.002

[1] In distilled water. [2] In N/50 H_2SO_4.

on the surface in and around the hot zone, also called "roughening" or "frosting" (Fig. B 10-103, I). With lead glass, which is readily reduced, this effect is accompanied by blackening at the same zone due to precipitation of metallic lead (cf. Fig. B 10-103, II). The cause of wrinkling is gradual leaching of alkalis or other components from the glass by atmospheric moisture which gives the surface a different composition and thus an expansion coefficient less than that of the core. When the work is cooled after flaming, fine folds or wrinkles develop on the surface. It is quite wrong to call this "devitrification", the term often used, because the effect has no connexion with crystallization. The error springs from the fact that the wrinkling is fine-grained and gives a whitish appearance similar to that of a glass with small crystalline inclusions. [10.2]

Particular attention should be paid to the storability of special glasses of low hydrolytic class (e.g. Kovar glass with very high B_2O_3 content, Table T 10–2, C, K 705);



I II

Fig. B 10-103 Wrinkling of glass surface produced by flame-working (JEBSEN-MARWEDEL)
I photomicrograph of surface; II wrinkling on lead glass, accompanied by lead-oxide reduction and hence blackening by metallic lead

6 months is the minimum requirement. After this time of storage in ordinary conditions the glass should not become matt (frosted) when worked in the flame. A short test is to take a 10 cm length of glass tube 10 mm dia., 1 mm wall, and suspend it for 1 hour over a constant-level, 7 cm-depth bath of boiling water, at a distance of 7 cm from the water. A 3-liter vessel is used to hold the water. The tube is then cut in half and both pieces are tested for wrinkling in the gas-torch, one when still moist from the bath and the other after 1 hour's drying at 105°. Neither section should "frost".

The outside of a hollow piece of glassware is always more resistant to weathering than the inside, since the former is "flame-polished" in the manufacturing process. An example of this is that completed hot-filament lamps being shipped in tropical areas show no signs of attack on the glass, but the inside of open bulbs of the same glass in the same consignment are fully weathered. Surfaces in direct contact with the working flame evaporate alkali, and also the SO_2 from the flame dealkalizes the glass. Some success in raising the hydrolytic resistance of Pb-free glass has been achieved by heat-treating in an atmosphere of SO_2 gas and H_2O vapor ([3]DOUGLAS, see also COUSEN, COWARD, KEPPELER, PEDDLE). A thin superficial layer of sodium sulphate is formed:

$$2\,SO_2 + 2\,Na_2O + O_2 = 2\,Na_2SO_4,$$

which can be easily rinsed off in water and the romaining low-alkali surface is much more resistant than the untreated one (cf. Fig. B 10-104, curves 1 and 2). Now if dilute HF is allowed to act on the surface for a time, the original composition of the glass is regained and the behavior in the presence of moisture reverts to normal (see Fig. B 10-104, curves 4–8). In the case of bulbs which have been given the SO_2 treatment, the usual HF wash (see 10.4. I (h)) has therefore to be carried out with some care.

[10.2]

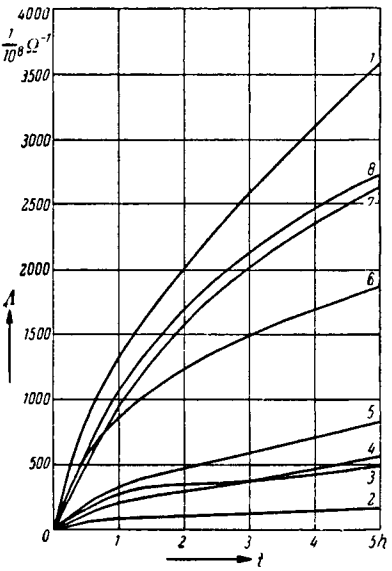


Fig. B 10-104 "Sensitivity" of glass bulbs after various treatments (SMELT)

Sensitivity index is given by rise in electrical conductance Λ of distilled water that filled the bulb, over 5 hr period

1 untreated;
2 SO_2-treated, washed in H_2O;
3 as 2, but washed $^1/_2$ min in 3% HF;
4 as 2, but washed 1 min in 3% HF;
5 as 2, but washed 2 min in 3% HF;
6 as 2, but washed 5 min in 3% HF;
7 as 2, but washed 11 min in 3% HF;
8 as 2, but washed 18 min in 3% HF

Resistance to alkaline solutions. Alkali hydroxides and carbonates affect glass in a way very different from water (see Fig. B 10-101 c). The Si—O—Si bonds are broken and new Si—O—Na and Si—O—H groups are formed which are transferred to the surrounding fluid. This time no gel is produced at the surface, which suffers much more damage than with water or ordinary acids. The time-dependence of leaching is linear. One cannot increase the chemical resistance of glass surfaces by treating with alkalis as can be done by acid treatment (see next section), in fact quite the reverse; any silica gel layer due to acid attack is dissolved, so that alternate exposure to acid and alkali affects glass chemically in a special way, dissolving it layer by layer.

Lye-resistance of glass has also been standardized (e.g. DIN 12122). The test-piece (sheet, rod or tube) has a definite surface area somewhere between 10 and 20 cm^2, known to 5%. It is cleaned in distilled water and alcohol, carefully dried, and weighed to 0.1 mg. It is then placed in a silver vessel and exposed for 3 hours to a boiling solution of 20.5 g NaOH and 27 g Na_2CO_3, the presence of the latter simulating more closely the true conditions under which glass is used, because CO_2 has a strong influence on the reaction. The solution is made up with 1 liter distilled water. The test-piece is then quickly dipped in very dilute HCl, rinsed with distilled water and dried. It is then weighed again. The weight loss is determined and calculated for a 100 cm^2 area. This value then gives the

classification corresponding to Table T 10–16. Class II glasses are still good for apparatus work. Table T 10–16 A shows some test results on different groups of glasses, carried out in the USA.

TABLE T 10–16. RESISTANCE OF GLASS TO LYES. CLASSIFICATION FOLLOWS DIN 12122

LYE CLASS	DESIGNATION	mg/100 cm² DISSOLVED OUT IN 3 HR
I	Weakly soluble	0–75
II	Medium soluble	75–150
III	Highly soluble	Above 150
IV(1)	Very highly soluble	(Above 400)

(1) Not standardized.

[10.2]

Figure B 10-105 shows an example of the corrosion depth produced by various concentrations of NaOH in a very inert borosilicate glass (CORNING Pyrex 7740). The great sensitivity of glass to alkaline solutions explains why water attack is accelerated even by low alkali content and rapidly increases with alkalinity, as shown in Fig. B 10-105 A, again exemplified by Pyrex.

TABLE T 10–16A. LYE RESISTANCE OF DIFFERENT GLASS GROUPS BY AMERICAN TEST METHODS ([3]SHAND)

TYPE OF GLASS	LOSS IN WEIGHT IN METHOD A(1) (mg/cm²)	LOSS IN WEIGHT IN METHOD B(2) (mg/cm²)
Soda-lime, sheet	0.8	0.18
Soda-lime, hollow-ware	0.8	1.5
Soda-lime, lamp bulbs	1.1	1.1
Lead, electrical use	1.6	0.25
High-lead	3.6	0.81
Alumo-borosilicate, apparatus	1.0	0.13
Low-expansion borosilicate (e.g. Pyrex)	1.4	0.12
Low-loss borosilicate	3.45	0.77
Borosilicate, W sealing	3.87	1.4
Alumosilicates	0.35	0.17
Alkali-resistant	0.09	0.03
Vycor (96% SiO_2)	0.9	0.07

(1) 6 hr in 5% NaOH at 100 °C.
(2) 6 hr in N/50 Na_2CO_3 solution at 100 °C.

Resistance to ordinary acids. The usual mineral acids (HCl, HNO_3, H_2SO_4) affect glass in the same way as water. Alkali components are rapidly leached out of the surface; the exposed SiO_2 gels by reagent-water absorption and protects the surface from further attack. In many cases, therefore, attack by acids is less than that by pure water. Only if the glass contains very acid-soluble components does the effect exceed that of water;

this is the case with glasses of high Al_2O_3 content. Sial glass is very chemically resistant and contains 6% Al_2O_3 (see Table T 10–2, C, and Table T 10–4, C); the ratio of amounts leached out by water, 20% HCl and 5% NaOH is 1 : 2 : 45.

There is also a standard for acid resistance of glass, but much greater surface areas have to be exposed in testing because attack by acids is slight. In the DIN 12116 process, several glass plates or tubes amounting to about 200 cm² have their total area determined to 5%; they are then washed in distilled water and alcohol and dried. They are weighed to 0.1 mg overall and immersed for 3 hours in boiling HCl (20 w/o, γ_{20} = [10.2] 1.100 g/cm³). They are washed again in distilled water and dried, and the weight loss

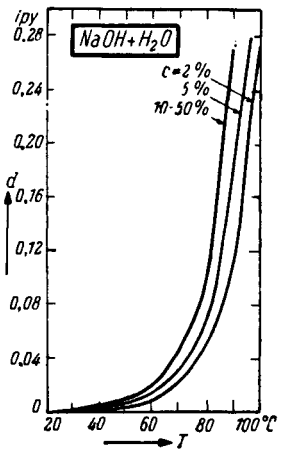


Fig. B 10-105 Corrosion depth d of aqueous NaOH of various concentrations c on Corning glass 7740 (Pyrex), as a function of temperature T ([1]CORNING)

For attack by other reagents use the following approximate factors to calculate from the figure: KOH, 100%; LiOH, 50%; Na_2CO_3, 20%; NH_4OH, 5% ipy (in./year)

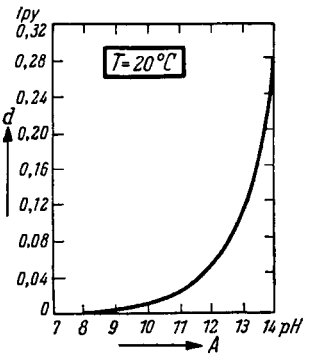


Fig. B 10-105A Penetration depth d of water containing alkali in Corning glass 7740 (Pyrex) at 20°, as a function of the alkalinity A ([1]CORNING); ipy = in./year

is measured and converted to the equivalent for 100 cm², the basis for classification (Table T 10–17).

Table T 10–17A gives some results on acid resistance of groups of glasses according to the test methods usual in the USA.

Behavior in the presence of HF and phosphoric acids. The effect is similar to that fo alkalis. Both acids break the Si—O—Si bond and in the first case volatile silicon fluoride is formed, in the second silicon phosphate. The solubility of glass in HF or its vapor is used frequently in cleaning contaminated surfaces and in frosting or etching, e.g. for printing letters on the glass. See Sections 10.4.I (h) and XVII–XXI for further details.

Phosphate glass without SiO_2 or B_2O_3 content can be resistant to HF, liquid solution or vapor-phase, but as a rule shows poor weathering characteristics. The composition of a commercial HF-resistant phosphate glass is given in Table T 10–2A, No. 7. This glass can be drawn to tubes and worked in the flame in the ordinary way.

Reaction to metallic vapors. It has already been mentioned in the section on UV transmission (10.2.XVI) that there is a direct effect of Hg ions on this parameter in addition to solarization by UV. After exposure in low-pressure Neon tubes where Hg vapor is mixed with gas filling, many types of glass blacken because of Hg ions. Of the soft glasses, high electrical resistance types have proved the best, in particular Pb-free

TABLE T 10–17. ACID-RESISTANCE OF GLASSES, ACCORDING TO DIN 12 116

ACID CLASS	DESIGNATION	mg/100 cm² DISSOLVED IN 3 HR
I	Acid resistant	0–0.7
II	Slightly acid-soluble	0.7–1.5
III	Medium to strongly acid-soluble	Above 1.5
IV(1)	Very acid-soluble	(Over 20)
V(1)	Extremely acid-soluble	(Over 200)

(1) Not standardized.

[10.2]

baryta glass (see Table T 10–17B); Pb glass, although suitable, tends to discolor from Pb reduced out in forming tubes.

Attack by alkali vapors on ordinary silicate glass is very strong, and the smaller the alkali atom, the stronger the attack; Li and Na have more effect than K, Rb or Cs. This has to be watched in the case of luminous tube lamps which contain alkali metal vapors

TABLE T 10–17A. ACID-RESISTANCE OF VARIOUS GLASS GROUPS, TESTED BY AMERICAN METHODS(1) (SHAND)

TYPE OF GLASS	WEIGHT LOSS (mg/cm²)
Soda-lime, hollow-ware	0.05
Soda-lime, lamp bulbs	0.01
Lead glass, electrical use	0.02
High-lead glass	Destroyed
Low-expansion borosilicate (e.g. Pyrex)	0.0045
Low-loss borosilicate	0.02
Borosilicate, W sealing	Totally lixiviated
Alumosilicates	0.35
Alkali-resistant glass	0.008
Vycor (96% SiO_2)	0.0005

(1) 24 hr in 5% HCl at 100 °C.

at high operating temperatures. Lead-silicate glass is particularly sensitive and is therefore not used for alkali photocells or sodium vapor lamps. Ordinary glass in a sodium lamp, that must run at about 270°, soon blackens on the inside from reduction of SiO_2 to metallic Si, and the Fe content produces a brown discoloration. However, alkali-resistant glasses have been made which are characterized by low SiO_2 and Fe contents, but have substantial amounts of B_2O_3 and Al_2O_3 (see Table T 10–17B). These glasses,

many of which unfortunately have very short softening range, do not exhibit discoloration even after long periods of operation, or only to a small extent.

High-boron sodium-resistant glasses are very corrosive when molten, and must therefore be fused in Pt crucibles to guard against impurity take-up (especially Fe). They are also poorly resistant to weathering (moisture in particular) and are only used as internal sheathing glass (25–75 μ thickness); see, e.g., Table T 10–2, E 3, Na-10 glass of the GEC, Wembley, in X 8 soda-lime glass made by the same firm (properties of the latter in Table T 10–4, E 3). The sheath glass is inserted in a thick tube of ordinary

[10.2]

TABLE T 10–17B. COMPOSITION OF A FEW GLASSES RESISTANT TO METALLIC VAPORS ([2]KNAPP UNLESS OTHERWISE STATED IN FOOTNOTES)[6]

RESISTANT TO	SiO_2	B_2O_3	P_2O_5	Al_2O_3	Na_2O	K_2O	CaO	BaO	MgO	MANUFACTURER
Hg	60	10	—	—	20	—	10	—	—	PHILIPS
Hg	53.7	—	5	22	—	—	13.5	5.8	—	BTH
Hg	8	40	—	10	11	—	—	31	—	COMP. DE LAMPS
Na	—	22.5	—	25	—	1.5	18	33	—	SCHOTT (3061 III)
Na	7.3	36.6	15.1	22.5	—	—	5.5	—	13	BTH
Na	5	39	16	23	—	—	5	—	12	(1)
Na	21.5	40	—	22	6.5	—	10	—	—	CORNING
Na	8.0	48	—	24	14	—	6	—	—	GEC
Na	5.0	25	—	25	6	2.5	—	36.5	—	OSRAM
Na	22.9	41.3	—	21.2	4.8	0.8	9.0	—	—	(3) (0.1 Fe_2O_3)
Na	—	36	—	27	—	—	—	27	10	(4)
Na	—	60	—	15	13	—	12	—	—	(5)
Na	25.8	49.6	—	11	4	—	9.6	—	—	(2)
Cd, Mg	57	—	—	20	—	—	—	—	23	PHILIPS
Cd, Mg	78	12	—	10	—	—	—	—	—	PHILIPS
Cd	55	15	—	30	—	—	—	—	—	PHILIPS
Cs	55	30	—	15	—	—	—	—	—	OSRAM

(1) Data from [6]STANWORTH (BTH). Sheathing glass, $\alpha = 50 \times 10^{-7}$ (1/°C) for borosilicate base glass BTH-C 40 (Kovar glass) of composition 66% SiO_2, 24% B_2O_3, 2% Al_2O_3 and 8% alkali oxides.

(2) SEWIG.

(3) LAPORTE.

(4) [2]SCHMIDT.

(5) From source not now identifiable.

(6) See also Table T 10–2, D 15, and E 3, also Table T 10–2A.

soda-lime glass and the combined tube is drawn down to small diameter. When leads are sealed into the main glass of Na-vapor lamps, the seal area has to be protected from Na attack either by MgO paste coating (see 20.6.V) or by a highly insulating, Na-resistant glass (e.g. sheathing glass SS 3, GEC, Wembley, Tables T 10–2 and T 10–4, E 3) which is fused to the seal ([1]MANNERS). Another way is to coat the inner wall of the discharge device, after forming, with a borate enamel and then fuse this layer to the envelope.

Besides Hg- and Na-resistant glasses, some which are resistant to vapors of Cd, Mg and Cs have been developed (see Table T 10–17B).

10.2.XXI. *Selection of Glass for Various Applications*

(Cf. also [1]DOUGLAS, [1]SPÄTE, Table T 10–4, columns headed "designation" and "notes", and Table T 10–18)

Hot-filament lamps, radio tubes. Envelopes: lime magnesia silicate; opal glass bulbs; fluoro-lime zinc silicate (see Table T 10–10B); feet, pump-stems, rod; lead silicate with 20–30% PbO.

High-power filament lamps, projector lamps. Lead borosilicate, e.g. hard tungsten glass.

[10.2]

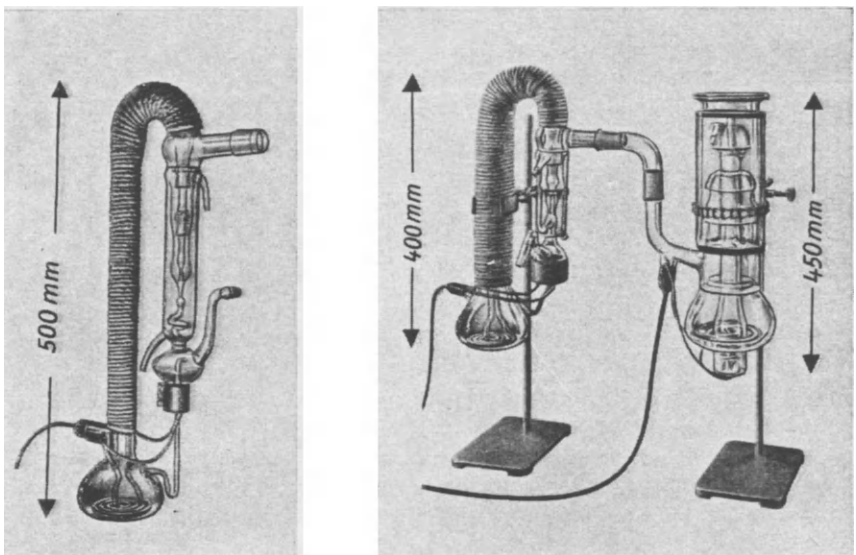


Fig. B 10-105B HV pumps made of Duran glass 50 (Manufacturer: JENAER GLASWERK SCHOTT UND GEN., Mainz)

I 3-stage Hg vapor ejector pump "3 Q 5" with heatable condensate trap; forevacuum needed = 15 Torr (water-jet pump); ultimate better than 10^{-6} Torr; pumping speed 5 liters/sec at 10^{-1} to 10^{-2} Torr; 500 W heater-power

II 3-stage oil booster pump "3 B 4" with heatable condensate oil separator; forevacuum needed = 4 Torr (single-stage rotary oil pump); ultimate *ca.* 10^{-6} Torr with LEYBOLD special oil L 50; pumping speed 4 liters/sec at 10^{-1} Torr; 550 W heater-power

III 3-stage oil diffusion pump "3 Oe 100" with fractionating section, removable jet system and flat sealing flange; forevacuum needed = 0.1–0.4 Torr (2-stage rotary oil pump, or booster pump (see II) + 1-stage rotary oil pump); ultimate 5×10^{-6} Torr with LEYBOLD oil "F"; speed 100 liters/sec at 10^{-3} Torr and 80 liters/sec at 10^{-6} Torr; 500 W heater-power

Amplifier tubes, small transmitter tubes, gas-filled hot-cathode rectifiers. Envelopes, solid bridges; medium-hard Thüringer apparatus glass (alumo-lime silicate); feet: 20–30% lead silicate glass.

Short-wave tubes: feet; low-loss glass, e.g. CORNING 7070, or Czech glass K 707.

TV tubes with glass cone. Neck and envelope including picture window: medium-hard alumoborosilicate; foot: lead glass. For tinted neutral glasses see Table T 10–2, A4.

TV tubes with metal cone (diffusion-chromed steel) (see 6.5.VI): neck: Fe-sealing glass containing Pb; window: Pb-free Fe-sealing glass (see Table T 10–4, e.g. H).

TV projection tubes. Window: X-ray tube glasses containing Ce.

TABLE T 10–18. THE CHIEF FILAMENT LAMP BULB-GLASSES ([1]KNAPP)[1]

CODE	MANUFACTURER[2]	TYPE OF GLASS	SEE TABLE T 10–	
			2	4
I. Clear glass bulbs, soft			PAGE	PAGE
105	OSRAM	Magnesia	12	40
584 d	OSRAM	Medium hard Thüringer	12	40
1065	MOOSBRUNN	Lime magnesia	—	64
B	TUNGSRAM	Magnesia	—	—
[10.2] 2	USSR	Bulb	22	66
C 19	BTH	Soda-lime	16	56
0080	CORNING	Lime	8	28
II. Opal glass bulbs, soft				
140	OSRAM	White fully opal	12	40
29	USSR	White opal	22	—
C 6 W	BTH	White opal	—	—
630	CORNING	Opal	—	—
219	OSRAM	Yellow, fully opal	—	—
221 a	OSRAM	Orange, fully opal	—	—
223	OSRAM	Red, fully opal	—	—
III. Tinted glass bulbs, soft				
586 g	OSRAM	Daylight, standard	—	—
C 19	BTH	Daylight	(16)	(56)
583	CORNING	Daylight	—	—
656 d	OSRAM	Wine red	—	—
656 e	OSRAM	Dark wine red	—	—
672 o	OSRAM	Dark-room red	—	—
672 n	OSRAM	Illumination red	—	—
C 4 R	BTH	Red	—	—
255	CORNING	Red	—	—
596	CORNING	Red	—	—
542	OSRAM	Amber yellow	—	—
C 19 Y	BTH	Yellow	(16)	(56)
370	CORNING	Yellow	—	—
240	OSRAM	Cornflower blue	—	—
662 b	OSRAM	Turquoise	—	—
C 19 Bl	BTH	Blue	(16)	(56)
538	CORNING	Blue	—	—
537	CORNING	Photo-blue	—	—
641 c	OSRAM	Illumination green	—	—
C 19 G	BTH	Green	(16)	(56)
432	CORNING	Green	—	—
IV. Special glass bulbs				
550	OSRAM	UV transparent, untinted	—	40
835 a	OSRAM	UV transparent, Hg-resistant	—	42
594	OSRAM	UV transparent, pale blue	—	40
55	USSR	UV transparent	22	66
C 17 BW	BTH	UV transparent, bright blue	—	—

TABLE T 10–18 *(continued)*

CODE	MANUFACTURER[2]	TYPE OF GLASS	SEE TABLE T 10–	
			2	4
			PAGE	PAGE
C 18 BW	BTH	UV transparent, dark blue	—	—
982	CORNING	UV transparent, lime glass	—	—
640 a	OSRAM	IR-transparent black glass	—	42
187	OSRAM	X-ray absorbing, clear	—	—
689 a	OSRAM	X-ray absorbing, black	—	—
23	USSR	X-ray absorbing	—	—
009	CORNING	X-ray absorbing	—	—
122 p	OSRAM	Resistant to Hg vapor, clear	—	40
C 21	BTH	Resistant to Hg vapor	—	—
C 10	BTH	Resistant to Na vapor	—	—
714	CORNING	Resistant to Na vapor	—	—
3061 III	SCHOTT	Resistant to Na vapor	13	52
V. High softening-point, clear glass bulbs				
394 b	OSRAM	Stated to be very heat-resistant	—	40
742	OSRAM	Alkali-free hard glass	12	42
40	USSR	Hard glass	22	66
C 53	BTH	Ignition glass	17	56
7740	CORNING	Pyrex	8	30
1720	CORNING	Alkali-free ignition glass	8	—

[10.2]

(1) See Chapters 30 and 32 for metal-sealing glasses.

(2) BTH = British Thomson-Houston. USSR = Russian bulb glasses.

X-ray tubes. Envelopes: X-ray glass + Ce (see Table T 10–4, A 3), borosilicates; windows: LINDEMANN glass; shielding glass: high-lead.

Electrometer tubes. Special high insulation resistance glass.

High-voltage rectifiers or transmitter tubes. Borosilicates, e.g. tungsten glass; for Housekeeper seal tubes: Thüringer apparatus glass; with Kovar seals: special Kovar glasses.

Hg-vapor rectifiers. Envelopes: Thüringer apparatus glass, also for seals of FeNi 50/50 or Pt; borosilicates, e.g. Mo glass for Mo seal-ins, Kovar glass for Kovar seal-ins.

Luminous tube lamps. Envelopes: lime silicates, borosilicates, Lumophor glasses (cf. 15.4.V), Hg lamps: baryta glasses (see also Table T 10–17B).

UV-lamps. Envelopes: glass low in oxides of Fe and Ti, lime-zinc, or borosilicates, or phosphate glasses.

Na-vapor lamps. Na-resistant alumo-borosilicates (see Table T 10–17B).

Photocells. Low-alkali Thüringer apparatus, or borosilicate glasses (e.g. tungsten glass).

Thermometer. Glasses with low depression-constant (see Table T 10–7).

Pumping equipment, McLEOD manometers, glass diffusion pumps. Thüringer apparatus glass, and nowadays also very hard glasses (see Fig. B 10-105B).

Metal sealing glass. See Chapter 30. Compositions in Table T 10–2, properties in Table T 10–4.

Graded seal (intermediate) glasses. For joining glasses of different expansion coefficients. See Tables T 10–2, D 9, T 10–4, D 8 and D 22.

10.3 Glass-working Processes

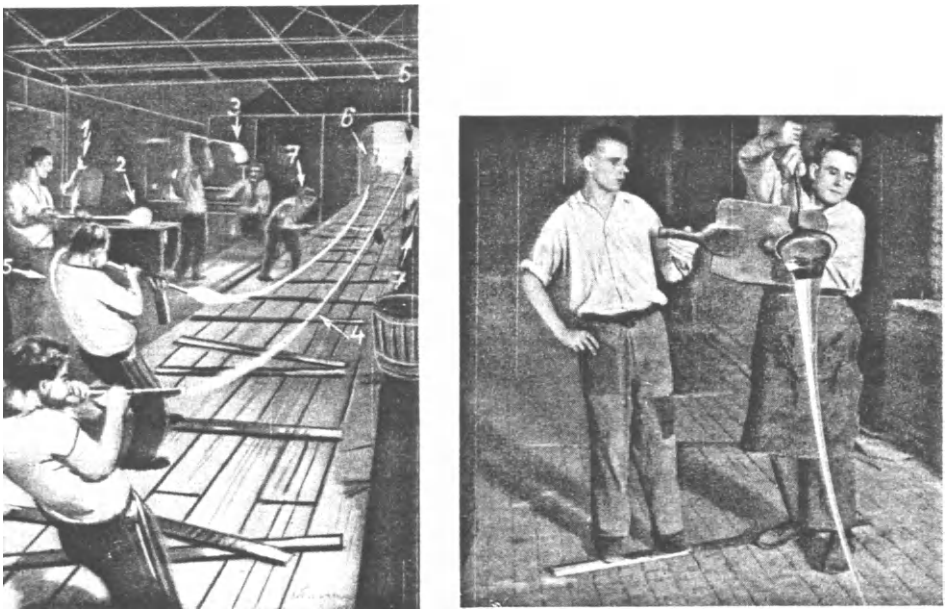
10.3.I. *Forming the Raw Glass; Preparation of Semi-finished Products in the Works*

(DRALLE, JEBSEN, [1]SCHMIDT, [3]SPÄTE, [2]VOLF)

The high-vacuum industry gets its glass in the form of semi-finished products, rod, tube or bulbs, supplied by the glass-works and automatic production plants.

The manufacture of rod and tubing even today is partly a hand operation, especially with hard-glass tube; Fig. B 10-105c shows the kind of process. The glass-blower

[10.3]



I II

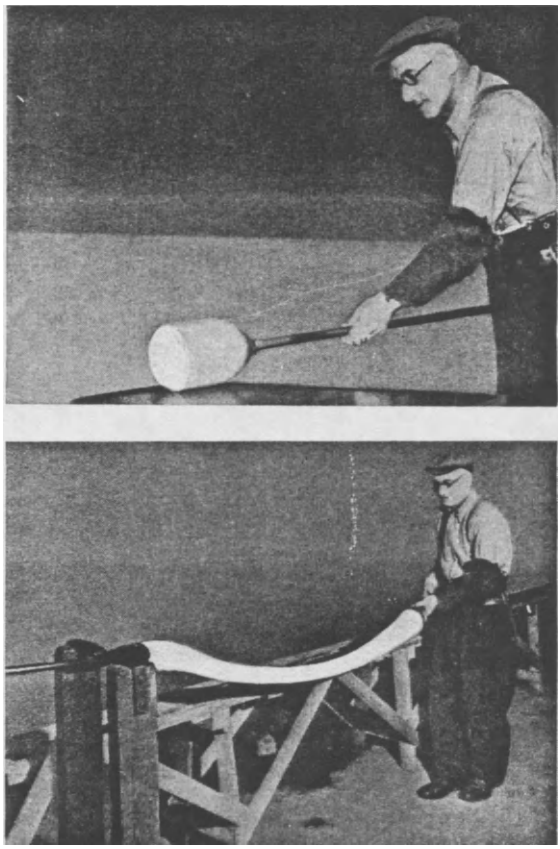
Fig. B 10-105c Manual drawing of glass tube and rod ([1]SPRINGER)

I tube drawing: *1* taking glass from the pot; *2* kneading the gather: *3* insertion of the hoit by the tube drawer into the gather; *4* tube drawing on the draw-way. The goffer (*5*) blows air continuously into the blowing iron which he turns at the same time, and the footmaker (*6*) pulls out to the tube as it forms, often to as much as 50 m or more. The cooling assistant (*7*) fans air against any overheated part of the tube to produce an even diameter while it is drawn

II solid glass rod being drawn

(goffer) employs a pipe made of iron ("blowing-iron") and provided with a mouth-piece to take a definite amount of glass from the pot of molten material and kneads the so-called "lump" or "gather" on a plate or morver. When this has removed the gaseous inclusions and the lump is evenly distributed over the pipe head, a second man, the tube-drawer (footmaker), puts a "handle-iron" (boit) into the lump opposite the pipe. Both men now walk away from each other and, as the boit and pipe are kept turning and the glass-blower blows into the pipe, the glass is drawn to a tube up to 50 m long or more. Obviously it is not possible to maintain the same diameter over the whole length; after cutting into sections it is sized according to diameter. Figure B 10-105d shows a similar process for making opal glass tubes of larger diameter for tubular lamps.

The DANNER drawing machine is based on the manual method and handles larger outputs. Glass runs from a crucible into a downward-sloping tube which is rotating (pipe, see Fig. B 10-106) with a suitable viscosity, fixed by the temperature of the stream of glass (see Fig. B 10-107). The pipe is covered with a firebrick sleeve and is flushed with compressed air when tubes are being drawn to prevent collapse of the glass (cf. Fig. B 10-106, I). When only 3–5 m from the pipe, the glass tube has enough strength to be drawn slowly through an annealing oven and over about 50 m of conveyor track on rolls and asbestos strip. At the end of the conveyor, the moving tube is cut to length by nicking with high-speed steel slitting-wheels or carborundum stone and then applying thermal or mechanical stress. A grab places the lengths in a sorter which drops them into an appropriate magazine after sizing. A DANNER machine can produce tubing up to about 70 mm dia. and rod up to



[10.3]

Fig. B 10-105 D Making large-diameter opal glass tube by hand (courtesy of GEC-OSRAM, Wembley, England)

Above: making the gather. *Below:* tube drawing; left (on the stand) is the pipe into which air is being blown; on the right is the boit which is turned continuously while the tube is being drawn

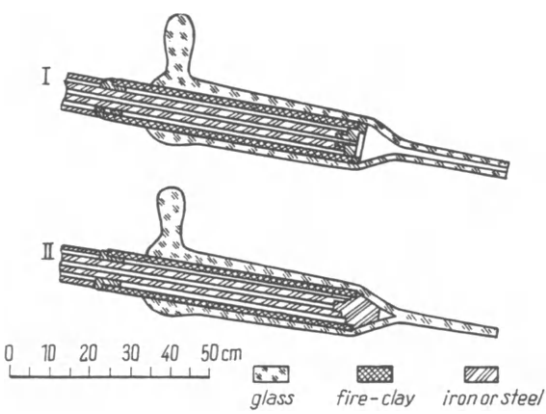
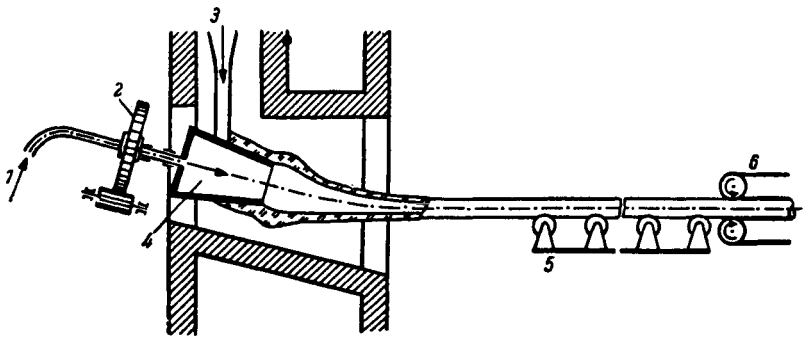


Fig. B 10-106 Cross-section of the blowing pipe of a tube-drawing machine (I) and a rod-drawing machine (II). See also Fig. B 10-107 for overall of the pipe in tube-drawing

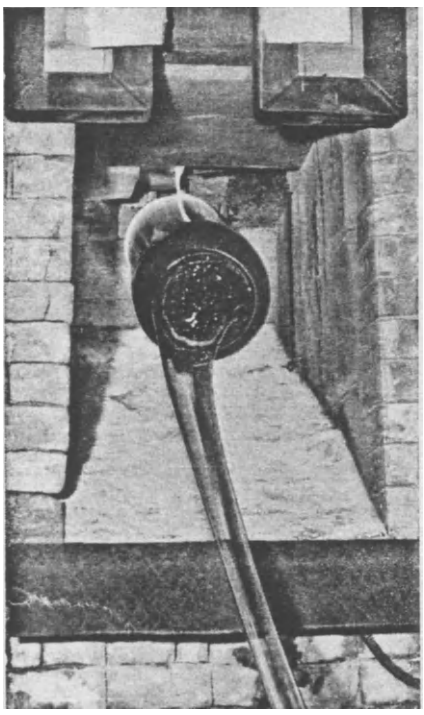
30 mm dia. The draw-rate is 10–100 m/min. Recently, vertical-feed machines have also been developed and put into operation.

For the one-off manufacture of hollow-ware, use is made of separate molds of cast-iron or some other less oxidizable metal or even of wood for small-scale production. The

[10.3]



I



II

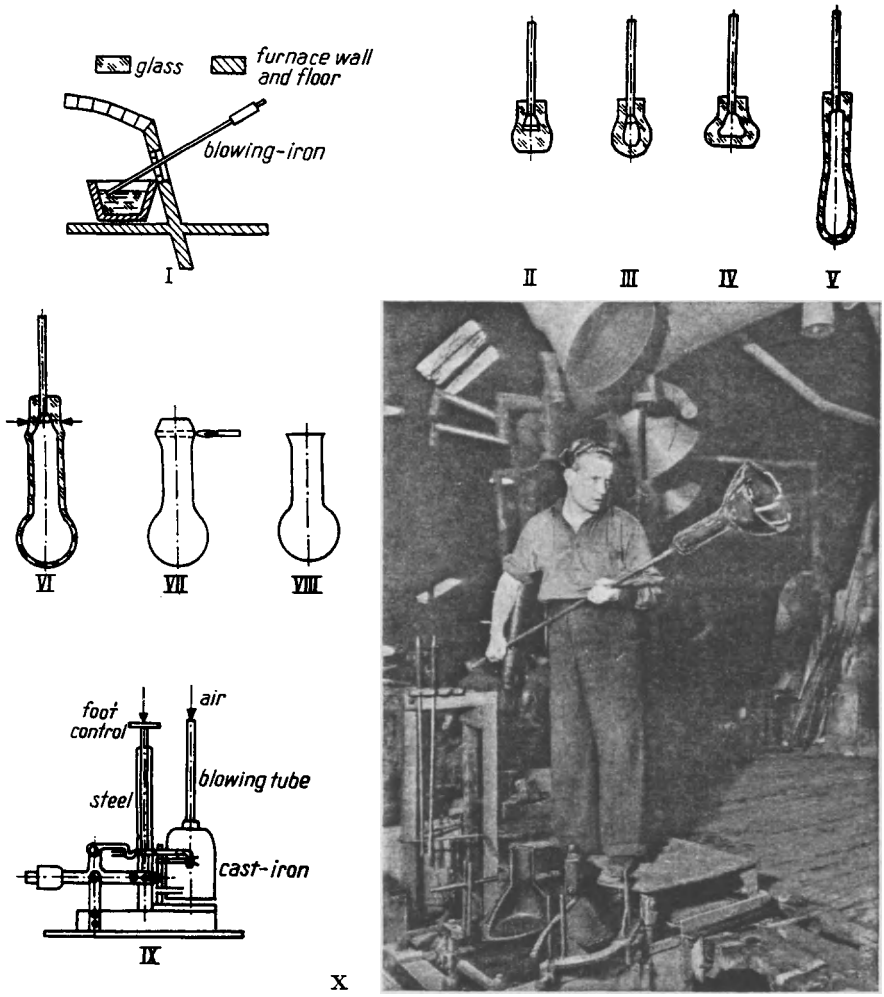
Fig. B 10-107 Viscous-flow discharge of glass from the pipe of a tube-drawing machine

I diagram: *1* hot compressed air; *2* drive; *3* glass stream; *4* conical pipe of heat-resistant steel; *5* transport rollers; *6* draw-rolls

II photograph courtesy of GEC-OSRAM, Wembley, England. In the foreground the glass tube runs over a 50 m draw-way and there slowly cools

glass lump or gather is held on the end of the pipe and blown into the mold (Fig. B 10-108). The glass is prevented from adhering to the mold by coating the inside with oil or aqueous graphite suspension (see also pre-treatment for pressure molding below, pp. 173–4), so that as the glass is blown, the lubricant (so-called) evaporates and

gives a thin gas layer between glass and mold which prevents sticking. If the work-piece is radially symmetrical it can be rotated in the mold while blowing proceeds and this yields a smoother, chord-free or streak-free surface. Large pieces must be made in



[10.3]

Fig. B 10-108 Blowing of individual pieces of glass hollow-ware

I removal of glass from furnace; II–V shaping the gather on the blowing iron in air; VI blowing the bulb in the mold IX; VII–VIII stages after blowing; IX cast-iron mold with auxiliary equipment; X blowing a TV tube envelope; the glass-blower stands over the open blow-mold (courtesy of GEC-OSRAM, Wembley, England)

several stages (molds) or the glass is pre-pressed in a mold that matches the blowing-mold.

To a certain extent, the machinery well known in the manufacture of bottles and vessels served as a model for automatic manufacture of glass bulbs. The main problem with such machines is automatic mold-filling with a constant amount of glass. There

is a proven method for high-vacuum envelopes in which the desired amount is drawn from the glass furnace by a suction mold and fed to the pipe (Figs. B 10-109, B 10-110). This is the principle on which the rotary "Ivanhoe" machine of Fig. B 10-111 operates; there are 24 blowing pipes and the 24 hr day output is 90,000 bulbs. The process is briefly as follows: the sliding head *G* (Fig. B 10-110) has one or more suction molds

[10.3]

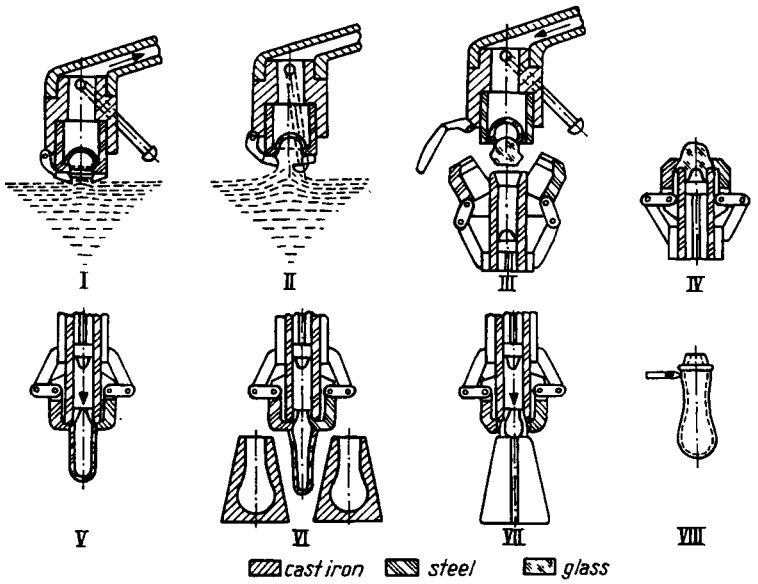


Fig. B 10-109 Manufacturing schedule for automatic bulb production

I empty suction mold on the molten glass surface in the "pot", air removed from the mold which is then (II) filled with glass; the lock closes; III the glass gather is fed to the pipe by forcing air into the mold; IV gather held on pipe, and mandrel inserted in gather centrally; V after turning the pipe a parison is formed by compressed air; VI parison dropped into an open mold; VII mold sealed and air blown into the parison; VIII mold opened, completed bulb fire-cut off

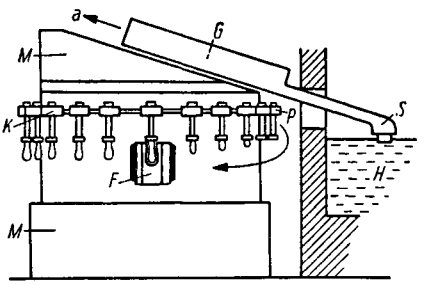
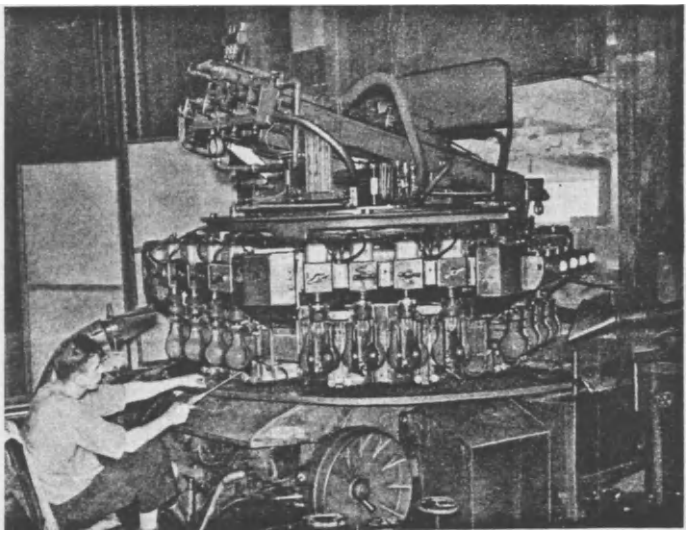


Fig. B 10-110 Design of fully-automatic bulb-manufacturing machine

K stepwise-rotating turntable; *G* sliding head, moves in direction of the arrow on the fixed-position section *M*; mold attached to front of sliding head, picks up glass from the furnace *H* and empties it into the pipe head at *P*. Blowing molds, as shown at *F* are aranged on the periphery of the turntable in large numbers

which withdraw a fixed amount of glass from the furnace by vacuum-suction. The head slides back until the mold lies above a pipe in the turntable. The gather falls into this pipe from the mold and as the turntable rotates the glass is blown to a bulb in a hinged sectional mold.

Figure B 10-111A shows the similar "Ohio bulb-blowing machine" which has a larger output than the Ivanhoe. Figure B 10-111B illustrates the construction of a very effi-



[10.3]

Fig. B 10-111 Fully-automatic Ivanhoe bulb-blowing machine with 24 blowing pipes fed from four suction molds. A 24 hr day's output of ordinary bulbs is about 90,000 (courtesy of OSRAM GmbH, Berlin)

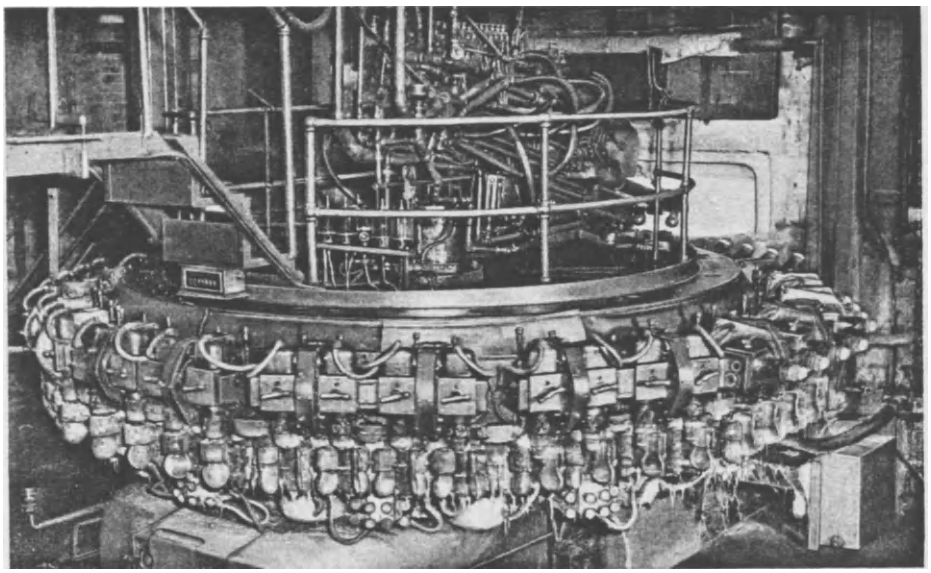


Fig. B 10-111A Ohio bulb machine with 48 pipes (courtesy of GEC-OSRAM, Wembley, England)

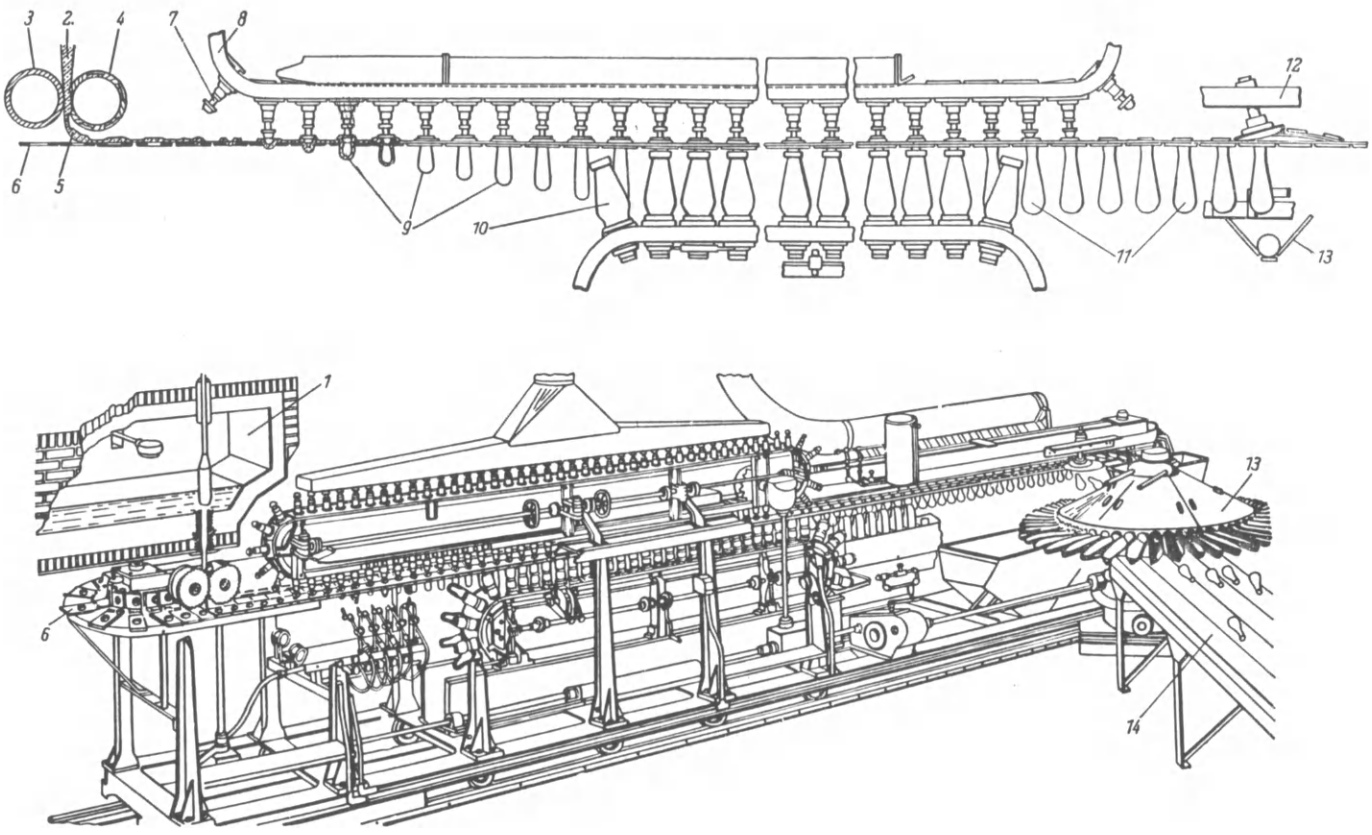
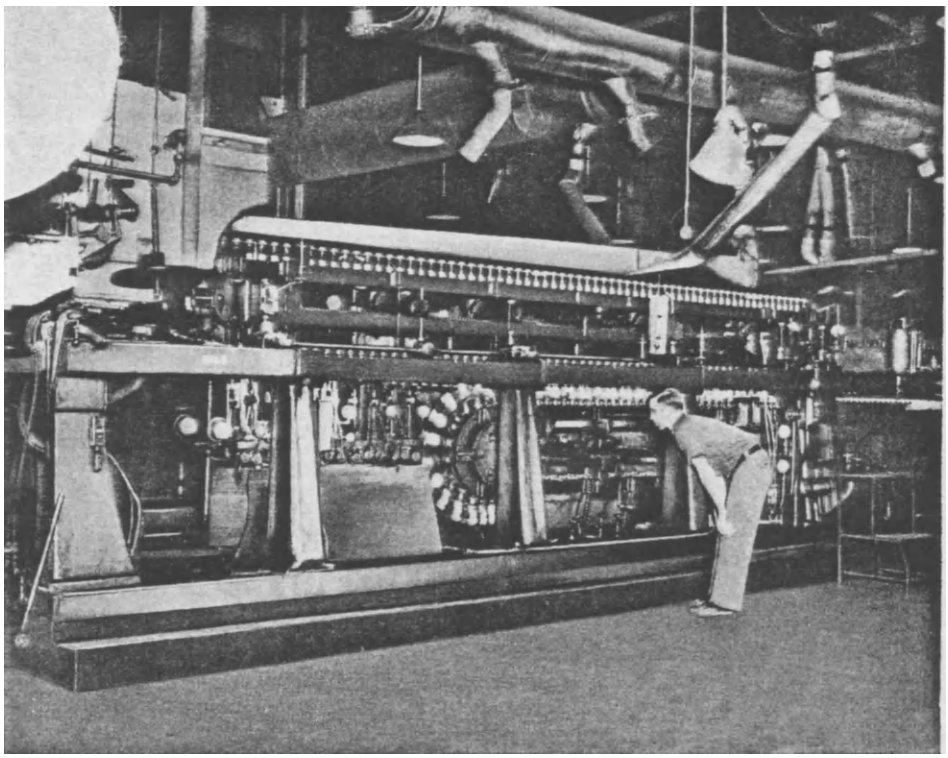


Fig. B 10-111 B_1 Construction of a RIBBON glass bulb machine of CORNING Glass Works. Daily output more than 1 million bulbs ([11]ANON.)

1 glass furnace; *2* cord of viscous glass; *3* smooth roll; *4* profile roll; *5* rolled ribbon of glass, with impressed blobs; *6* conveyor belt made of perforated metal plates; *7* blowing heads; *8* carrier belt for *7*; *9* glass bulbs blown through the holes in the conveyor belt; *10* split molds carried on conveyor below *6* and surrounding bulbs *9*; *11* finished glass bulbs; *12* separator; *13* take-off device; *14* conveyor for bulbs to annealing oven

cient type, the so-called "ribbon machine" of CORNING Glass Works. This has the astonishing output of 500,000 bulbs per day, with 70, 75 and 80 mm dia. for 75, 100 and 150 watt lamps. A smaller variation on the machine produces as much as 1800 per minute, about 2 million per day with dia. between 25 and 65 mm (miniature and 60 watt lamps); this is faster than a machine gun shoots bullets! Only one man is needed to operate the equipment.



[10.3]

Fig. B 10-111B$_2$ View of a Ribbon bulb-blowing machine of the CORNING Glass Works. Daily output more than 1 million bulbs ([11]ANON.)

In this machine, a cord *2* of glass flows from the furnace *1* and between two water-cooled rolls *3* and *4*. Roll *3* has a smooth surface, *4* has round pockets and this gives the viscous glass ribbon *5* a controllable series of humps or blobs. The ribbon lies on a conveyor belt *6* of perforated metal plates in such a way that each blob of glass comes over a hole. Blow-nozzle *7* is carried on a second belt *8* overhead and, as the belts travel, blows a hollow in each blob and then blows the glass of the blob through the hole to form bulbs *9* on the underside of ribbon-carrying belt. Split molds *10* carried on another conveyor below, then receive the bulbs. The molds rotate and give the bulb the proper outer shape. When the molds are reopened, the shaped bulbs *11* are cut from the rest of the glass ribbon by an intermittent separator *12* and fed by a rotating take-off device

via a conveyor belt *14* to the annealing oven. Belt *6* is freed of residual glass by cold-water quenching and the process begins again.

Finally, Fig. B 10-112 shows a bank of bulb-blowing machines developed and used by the PHILIPS Works in Eindhoven, Holland. Each has its own glass furnace. The viscous glass streams through a bottom-pouring orifice and is cut into sections of a given weight immediately below by a kind of shears. The sections drop into blowing pipes on a continuously rotating turntable, and gradually take on their final form as the turntable rotates; they are then ejected and fed into an annealing furnace by conveyor
[10.3] belt.

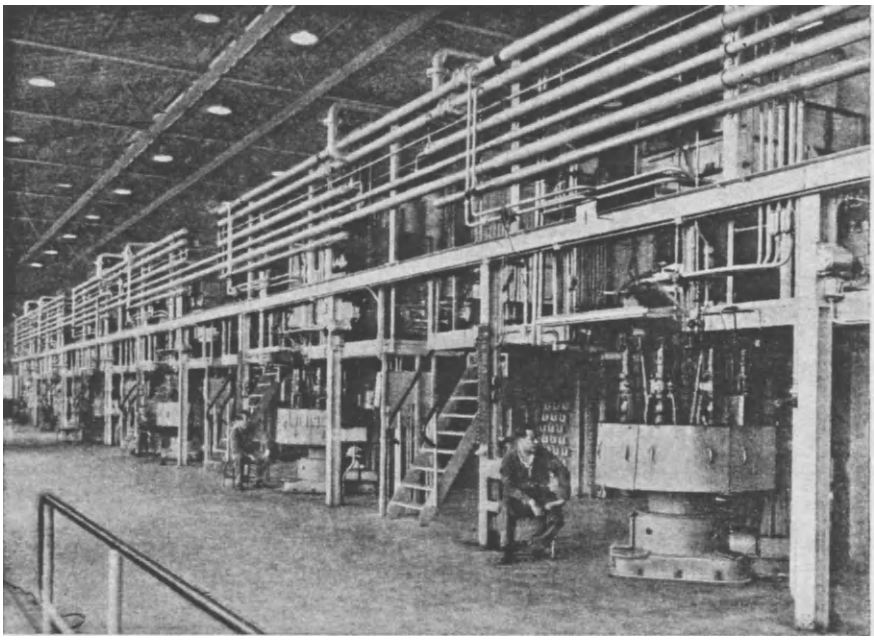


Fig. B 10-112 Bank of bulb-blowing machines (courtesy of PHILIPS). (Cf. [9]ANON.)
Associated furnaces of molten glass are on the gallery behind the machines. The raw feed to the furnaces also comes from the rear

Need for reliable operation of these large automatic machines and constant quality of glass product make it of great importance not only to retain consistency in the composition of the glass and in the heat applied but also to set the temperature of the molds correctly; this is achieved by thermal lagging or conduction. Heat input from the hot gather and the flame and conduction of heat in the molds only result in thermal equilibrium of the iron structure after prolonged running-in periods. Every production stoppage entails considerable loss in re-establishing equilibrium, and the machines are therefore allowed to run for as long as possible without interruption.

The blowing operation, particularly with large amounts of glass, can be carried out with steam rather than compressed air, under suitable conditions. One method is to place the work on moist asbestos and heat from the glass forms steam; or one can in-

troduce a few drops of water into the hollow in the gather and then close the pipe so that pressure of the steam so formed blows the glass.

Compared with metal stock, tolerances are large on semi-finished glass (rod, tube and bulbs), whether blown or drawn, whoever the manufacturer is; this is true in spite of automatic methods. A rough picture of feasible tolerances is given by Fig. B 10-112A and Table T 10–19.

Improved tolerance levels can be held on parts made in the works by molding under pressure. See pp. 195–6 for pressing of flat glass bases in electron-tube production, and [10.3]

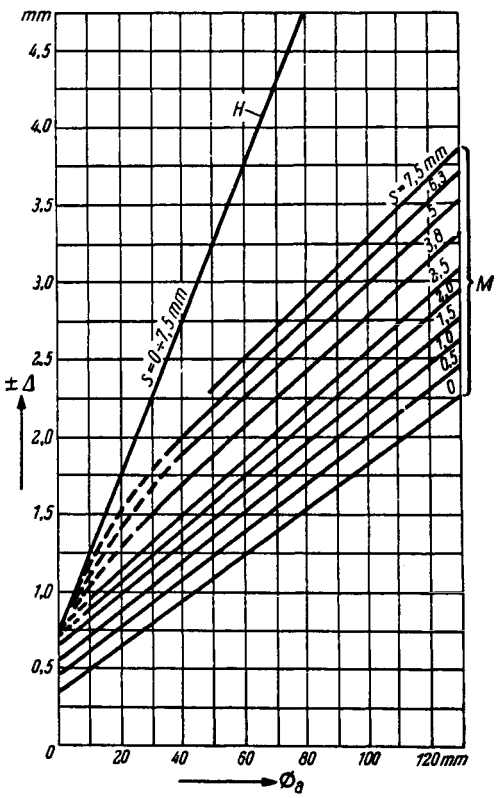


Fig. B 10-112A Permissible standard tolerance $\pm\Delta$ on O.D. (including ovality) of borosilicate tubing of wall-thickness s, plotted as a function of nominal O.D. Φ_a (²SHAND)

Curves M (for various wall-thicknesses s) apply to machine-drawn tubing, curve H (any wall-thickness s) applies to hand-drawn tubing

see Fig. B 10-137 and associated text for cast glass tube bases. Adhesion of glass to the surface of metal casting or press molds (dies) is best prevented either by a graphite film made by spraying with a colloidal suspension of graphite in water ("Aquadag") or in oil ("Oildag"), or brushing on a suspension of red lead oxide in a dope or lacquer and dusting the wet surface with fine carbon powder. The die is then dried at a slightly elevated temperature in air. See, e.g., MURPHY and 8.5.IV for further details.

"Long" glasses, which have a large temperature difference $\Delta = T_{soft} - T_{an}$, are the most suitable for press-molding, since solidification is not too rapid when cooling in molds; the glass should not have too high a working temperature or the die will oxidize and have a short life. Of low-expansion glasses, Kovar glass is the best; $\Delta = 233°$ and

$T_{work} = 1115°$. Press-molding of Supremax is difficult because although $\Delta = 215°$, $T_{work} = 1250°$ or above. Of glasses with α in the range 90–100 $\times$ 10^{-7} (1/°C), the best is Pb-glass which is relatively long; $\Delta = 200°$, $T_{work} = 975°$. Short soda-lime glass is not so good as lead; $\Delta = 180°$, $T_{work} = 1000°$. The very short borate glasses with more than 50% B_2O_3 are not suitable since their Δ is only 130°, even though T_{work} is about 600° ([1]SMELT).

TABLE T 10–19. STANDARDS IN MEASUREMENT TOLERANCES (mm) FOR SEMI-FINISHED GLASSWARE (AS USED BY SIEMENS-RÖHRENWERK 1944)[1]

[10.3]

FORM	DIAMETER	WALL	SOFT GLASS				HARD GLASS	
			HAND-DRAWN		MACHINE-DRAWN		HAND-DRAWN	
			DIA. ±	WALL[2] ±	DIA. ±	WALL[2] ±	DIA. ±	WALL[2] ±
Tube	Up to 3	0.5–1.0	0.2	0.15	–	–	0.2	0.15
[3]	3–12	0.7–1.5	0.4	0.2	0.4	0.15	0.5	0.25
[4]	12–25	1.0–2.0	0.8	0.3	0.6	0.15	1.0	0.3
	25–40	1.5–3.0	2.0	0.4	–	–	2.0	0.4
Rod	Up to 2		0.2		0.15		0.3	
	2–6		0.4		0.25		0.6	
	6–10		0.6				0.8	

[1] Cf. also Fig. B 10-112A.

[2] [2]SHAND states that CORNING Glass Works uses the following standard tolerances for borosilicate tubing of wall-thickness s:

(a) hand-drawn $\pm 0.30\,s$;

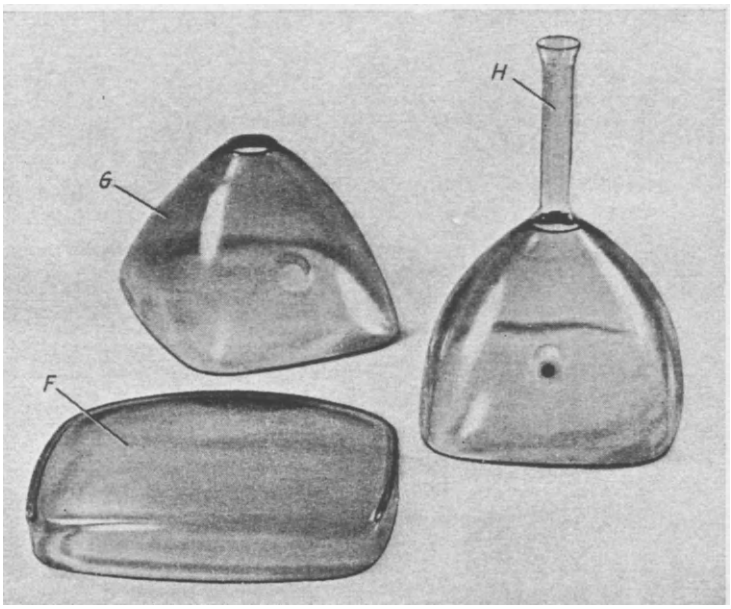
(b) machine-drawn $\pm 0.25\,s$.

[3] Commercial lengths are 1–1.5 m.

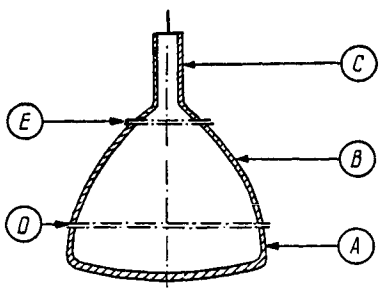
[4] Tubes with a calibrated I.D. of 1–50 mm and tolerance ± 0.01 mm are known as "KPG tube", made by SCHOTT UND GEN.; the O.D. has larger tolerances and the wall is therefore not quite constant.

It may be necessary that the pressing be absolutely free of air-bubbles, as in the case of the front face of TV tubes. In this event, the surface area of the pot or furnace from which the glass is drawn must be as large as possible compared with the charge, to facilitate escape of any air bubbles. In practice the ratio varies from 1 : 1 to 5 : 1, surface area (m^2) to glass charge (tons). It is worth drawing attention to the fact that with large picture tubes (screens over 17 in. dia.) to some extent it has become the practice to press-mold not only the face but also the cone and then (Fig. B 10-112B) fuse the screen carrier (A), the cone (B) and the drawn neck (C) together to make the tube. For reasons of economy, A and B are not lead glass, but special glasses with similar viscosity characteristics.

In the manufacture of cones for large TV tubes, press molding has been successfully replaced by a method in which the glass mass is centrifuged on to the inner wall of a heated mold. Figure B 10-112C shows the method, in which the tube neck is formed at the same time.



[10.3]



A press-molded screen panel

B press-molded cone, which can also be made by the centrifuge method (Fig. B 10-112c) with thinner wall than pressed version

C Pb-glass neck, drawn

D and *E* seams generally made by electrical resistance welding (Fig. B 10-161)

F and *G* press-molded panel and cone of a 17 in., 70° TV tube, SCHOTT glass 8196

H machine-drawn neck of SCHOTT Pb-glass 8095

(Photograph by JENAER GLASWERK SCHOTT UND GEN., Mainz)

Fig. B 10-112B Example of the application of pressed moldings in manufacture of TV tubes ([2]ROTTGARDT, [2]SMELT)

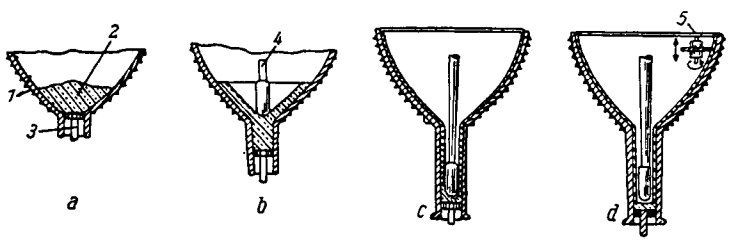


Fig. B 10-112C Stages *a* to *d* of centrifugal molding method of making TV tube cones with integral neck ([2]CORNING)

1 heated, rotating mold; *2* molten glass; *3* piston, can be lowered from below; *4* mandrel for forming neck; *5* shaping wheel to form the cone skirt

10.3.II. *Further Working of Semi-finished Glass by Thermoplastic Methods*

In the vacuum industry, working glass stock from the makers is carried out almost solely by thermoplastic processes, i.e. fusion forming by blowing, pressing, drawing or centrifuging. Chip-cutting or grinding of glass is exceptional.

Thermoplastic forming. Even today, the usual way is by direct contact between glass and burner flame; this means by thermal convection. In certain cases, however, radiant heat, resistance welding or arc welding are used. A point of fundamental importance here is that although drawing-off and casting or pouring glass in the works involve [10.3] temperatures at which viscosity is 10^2 P, and works blowing processes are carried out at viscosities of 10^3 to 10^7, glass-working of bulbs and tubes by the apparatus manufacturer is done at 10^5 to 10^{10}. Glass-glass or glass-metal sealing, however, is done at 10^3 to 10^4 P (see also Table T 10–20, note 2). The temperature to which glass is heated in this viscosity range depends essentially on shape and size of the work. The temperature is generally not higher than absolutely necessary, or the viscosity may become so low that the glass does not retain enough stiffness to keep its shape (after forming) under its own weight. It is also important to keep well out of the devitrification range (see 10.2.III) if possible, or to pass through it as rapidly as possible, which means that the glass should not be flame-worked for a longer period or at a higher temperature than necessary.

Flame-working. The chief source of flame gas is the city main, but this suffers from pressure drop in the complex manifold and lines to the various machines, and compressors are needed. To control constancy of calorific value, a recommended procedure in large works is to install a recording device to measure it and to have a binding supply-contract with the gasworks. See, e.g., WHITNEY on the question of the quality of city gas. In works where there is no gas main, one can work with propane-acetylene mixtures plus compressed air (see, e.g., ZIENER). Even hard glass can be worked in this way without a supply of oxygen. After the main gas-meter, a compressor must be installed to raise the pressure from 50 to 250 mm water gauge (i.e. from 20 to 100 in.). The gas is fed with compressed air at the burner, also from a central compressor, and the usual working pressure is $^1/_2$–1 atm gauge. The temperature of this mixture is insufficient for harder high-melting glasses, especially for quartz glass working, which require the use of oxygen, and hydrogen replaces illumination gas from the city main. It is also better to use oxyhydrogen gas if the sulfur content of the main supply, which can amount to 15 g/100 m^3, might poison cathodes. An example of this is sealing on the envelopes of miniature oxide-cathode tubes, and for the same reason city gas has sometimes to be replaced by propane, butane, or mixtures thereof. Illumination gas which contains sulfur compounds forms a white film of sodium or lead sulfate on soda-lime or lead glass. Although Na_2SO_4 can be easily washed off in water, removal of $PbSO_4$ presents some difficulty. In this case installation of a gas-purification train is recommended.

Table T 10–20 gives a rough survey of the various types of flame used and temperatures needed for the most common glass-working processes.

The burner. Choice of the best type is not simple and requires much experience. The following aspects are of prime importance in burner function:

TABLE T 10-20. SURVEY OF THE TYPES OF FLAME USED IN GLASS-WORKING, IN ORDER OF RISING TEMPERATURE ([5]ESPE)

MAX. TEMP. OF GLASS[1] (OR HEAT OUTPUT) NEEDED (°C)	FLAME TYPE	CHIEF USE	GAS CONSUMPTION ACCORDING TO BURNER SIZE (l./hr)
300–500	Sooty oil-flame	Tempering	
500–700	Yellow flame, no air feed	Annealing after forming	
$\leq$ 1000	Bunsen flame + air feed	Flame-polishing cut or fractured edges	City gas, 80–290
(770–3550 kcal/hr)	Blue flame with increased mixture (gas + air)	Tempering ovens	City gas, 185–850
	Blue flame + compressed air	Tempering ovens	City gas, 230–1050
800–1200[2]	Gas + compressed air burner	Soft glass working	City gas, 10–3200 Compressed air, 50–15,000
1400–1700	City gas + compressed air burner, with O_2 feed	Hard glass working	O_2, 450–700 City gas, 600–700
1600–2000	Oxyhydrogen flame	Working quartz glass	H_2, 1000–2700 O_2, 300–900

[10.3]

[1] This is the temperature of the work as estimated or determined by pyrometer, neglecting difference between true and black-body temp. The max. *flame* temp. at the hottest zone is obviously much higher and usually amounts to *ca.* 2000 for gas-air and 2900° for gas-oxygen mixtures ([1]RICHARDSON).

[2] The individual temperatures needed for most glass-working processes in vacuum technology are given in the following section of the table ([1]RICHARDSON):

PROCESS	EXAMPLES OF PROCESS	GLASS	VISCOSITY OF GLASS REQUIRED	TEMP. APPROX (°C)
Simple types	Glass-lathe work	Pb	$10^{5.5}$	800
Glass-metal seal	Pinch and press bases	Pb	$10^{3.8}$	1000
Glass-glass seal	Bulb-foot joining	Magnesia-lime to Pb	$10^{3.5}$	1050
Fire-cutting	Cut-off glass skirt Fig. B 10-138, *d*	Lime-magnesia	$10^{3.3}$	1140
Sealing off	Sealing and cutting off tube, e.g. pump stems	Pb	$10^{3.3}$	1100

(a) Shape of the flame: this is mainly determined by the type of burner, but also by the type of gas and its pressure and should be chosen so that the heat of the flame is concentrated on the desired portions of the work. Note that the hottest zone is 3–6 mm above the tip of the inner dark cone, but the coolest is at this tip.

(b) Naturally this must suit the glass and type of process (required viscosity), and is a function of the calorific value of the gas, the air/oxygen/gas ratio, and gas pressure.

(c) Character of flame: oxidizing for lead glass, reducing for alumosilicate.

(d) Heat developed: must be enough to bring the work to required viscosity in the time [10.3] dictated by the machine cycle or schedule. Glass-working practice in vacuum technology involves no less than 300 types of burner ([1]RICHARDSON): single orifice types with long flame focus, multiple orifice types with short focus and burners designed for O_2 addition, with flame splitters (Fig. B 10-113). Gas mixing (air, oxygen, city gas) usually takes place in a chamber just before the nozzle and splitter.

Several burner nozzles are often required to achieve the desired flame distribution. Figure B 10-114 shows a few standard designs of burner. The slotted nozzle type produces a knife flame (batswing) suitable for small-area heating; this contrasts with the round nozzle type which can give a pencil or a fat flame according to shape. Burners are often provided with ball joints which facilitate positioning of the flame on automatic machines. Mention should be made of a safety valve system for use with O_2, where the O_2 tap can only open after the gas and air supplies have been released, thus preventing the formation of explosive oxy-hydrogen gas (Fig. B 10-115). See, e.g., [8]ANON. and [1]RICHARDSON for further details of glass-working burners.

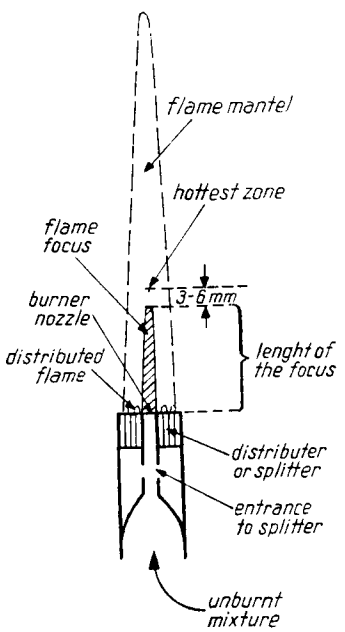
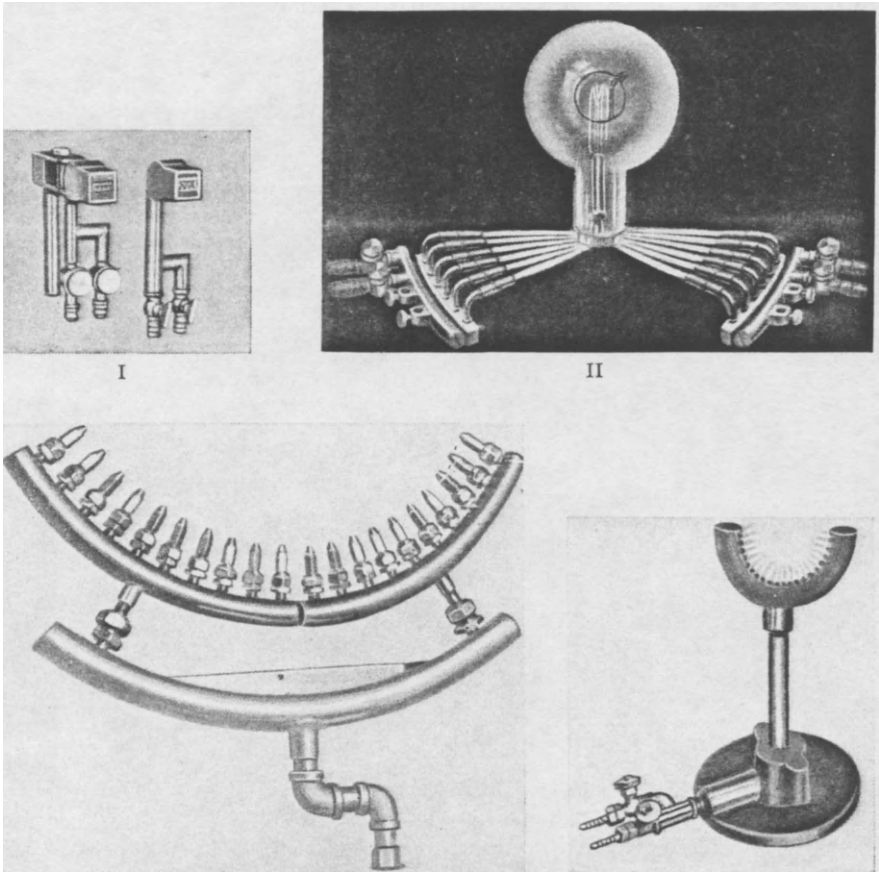


Fig. B 10-113 Diagram of the flame from a glass-working torch or burner ([1]RICHARDSON)

The glass-working process and the corresponding set-up of the burner at the start of operations must be such that a general warming of the glass piece in a brush flame takes place before localized heating of the area to be shaped; after forming, efforts should be made to cool the glass-work as slowly as possible in the brush flame to prevent excessive thermal stresses. In spite of such precautions, it is generally necessary to give glass formed by automatic machines a final anneal in so-called "tempering ovens" (see 10.3.VIII).

The working area. The shop where glass is worked in the open flame should be only moderately well-lit to assist flame-adjustment before starting the machines, for flames are poorly visible in bright light. Air extraction or too-rapid air circulation can endanger the work by sudden local cooling of the heated component and, in the case of glass-blowing machines, by deflecting the flame. For this reason such machines are often

surrounded by a partition which, especially if double, provides thermal lagging. The mechanical loads on glass-working machines are small compared with chip-cutting lathes so their life is relatively long, provided sufficient thought is given to insulation



[10.3]

Fig. B 10-114 Types of burner

I flat, for heating limited regions, city gas consumption 60–85 l./hr, compressed air 300–425 l./hr depending on width of burner head (made by GLADITZ GmbH, Schwäbisch Gmünd, Württemberg)

II cross-fire burner, up to 10 flames, individually movable, gas consumption 10–250 l./hr, compressed air 50–1250 l./hr per flame

III large ring-burner for sealing in the windows of TV tubes (made by EISLER ENG. Co.)

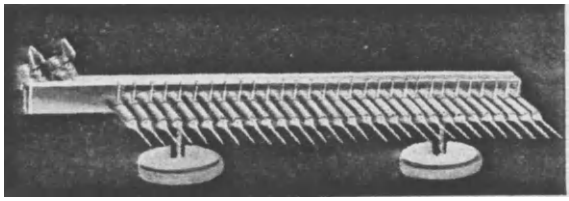
IV half-ring vertical burner, ring dia. 50–300 mm for air-gas or H_2—O_2 mixtures, made of cast-iron or Monel (made by EISLER)

of the moving parts from the heat. If great precision is required, machines should be of the ball-bearing type since bush or sleeve bearings are less able to stand large variations in temperature and cooling has to be provided. Any mechanical parts which operate directly in the flame must be of heat- and oxidation-resistant material (see, e.g., KALPERS, DARTNELL).

Oxygen and hydrogen are stored in and supplied from the usual steel high-pressure gas cylinders which are generally installed in a central position. The full cylinder pressure of 150 atm is reduced to 5. and the gases are fed down a branched main system to the individual working areas and set at the desired pressure at the burner by further reducing valves.

[10.3]

V



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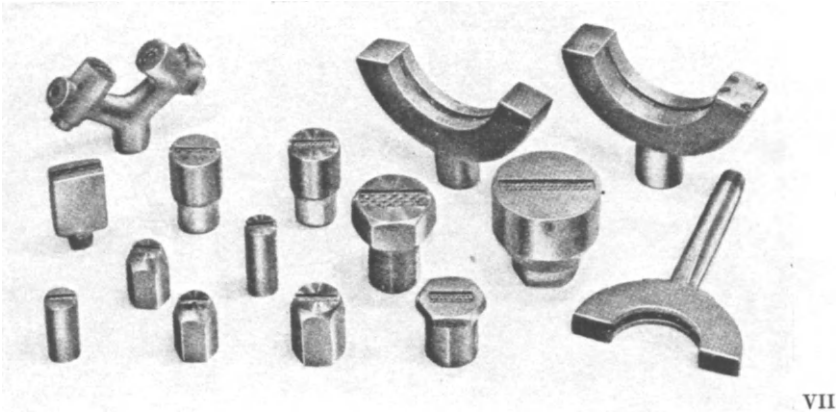


VII

Fig. B 10-114 (*continued*) Types of burner

V full-ring horizontal burner, other data as in IV (made by EISLER)

VI so-called split-feed burner with 20 or more parallel pencil flames, gas consumption 10 l./hr, compressed air 50 l./hr per flame (made by BORNKESSEL GmbH, Berlin W 30)

VII burners for making hollow-ware by machine (made by AMBEG, Berlin-Schöneberg)

It is often necessary to install purification and safety devices in the gas supply for glass-working. Bag-like filters may be provided in the city gas and compressed air lines in which oil and dirt from the compressors can be collected. Water traps in the city gas lines and flame-trap cartridges in the cylinder-gas lines have proved successful in avoiding flash-back.

The gas-tightness of lines and valves including any rubber tubes must be regularly checked. On safety grounds, open flames should be screened off wherever possible. In glass-working shops, adequate provision of protective clothing should be made for handling hot piece-parts; i.e. asbestos gloves and asbestos or leather aprons. Care should be taken that they are used properly.

10.3.II*a*. *Hand Working*

There are still many occasions even today when devices are made by experienced glass-blowers, especially vacuum apparatus, but also on small-scale tube production and in the manufacture of very large tubes such as glass rectifiers with Hg-vapor filling. The glass-blower may either use a fixed-position bench burner to work the glass, blowing air by mouth into the piece and turning it in the flame, or he may use a hand-torch to join other parts to the work-piece which is clamped in position, as in attaching anode side-arms to envelopes or completed tubes to a pump manifold. It should be absolutely forbidden to blow air from the mouth into tubes with degassed electrode assemblies, for [10.3] example blowing the joint when sealing a tube to the pump manifold. The glass-blower should work with oil-free dry air at *ca.* $^1/_2$ atm gauge from a reducing valve; it is best to

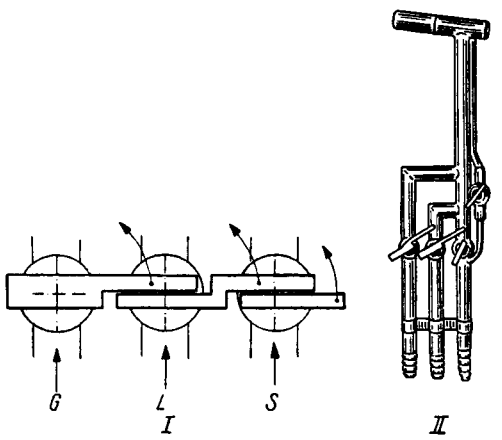


Fig. B 10-115 Safety interlock system for gas-taps

I diagram of arrangement: the order of opening is automatically enforced; *1* tap *G*, city gas or H_2; *2* tap *L*, air; *3* tap *S*, O_2; *II* production model of gas-air-oxygen blow-torch; gas *ca.* 700 l./hr, compressed air *ca.* 350 l./hr, O_2 *ca.* 700 l./hr

feed the air close by the valves on the hand-torch and provide a bleed-hole about 10 mm dia. in reach of the fingers holding the torch. When the hole is open, air escapes and the gauge pressure in the sealing area is nil; by closing the hole for a moment, or partly closing it, with the finger-tip, the air pressure in the tube can be controlled with almost as sensitive a "feel" as when mouth-blowing (see, however, page 212). For the technique of glass-blowing, which requires much practice and skill, refer to the many special works on the main aspects of the subject, e.g. BARR, [1]EBERT, HELDMAN, NOKES, STRONG, WEHNELT, WOYTACEK.

10.3.II*b*. *Glass-working by Machine*

The effort to make the relatively difficult manual procedures easier and cheaper led to the development of semi-automatic equipment, and, for very large-scale production, fully-automatic equipment. Efforts were also made to break down the complex processes of manufacture into fairly simple steps that could be accomplished by unskilled personnel (see, e.g., DAVIES, [5]ESPE, ZIMBER).

In every fully-automatic machine operation on semi-finished products, the series of steps applied to the same work-piece are programmed in advance and this programme is adhered to. The fabrication process on semi-automatic machines can be arbitrarily

altered within certain limits; for example, at certain critical stages in the schedule, the flame temperature can be adjusted by the operator to the item that is being worked at the time or the process time can be altered by accelerating or decelerating the carrier; however, restrictions are imposed on this, especially in the latter case, by the fact that in semi-automatic productions of many parts on the same machine, those in the preceding or succeeding stages will be affected. As the approved glass-working machines in vacuum equipment firms are automatic or semi-automatic multiple-position units, it follows that softening the work-pieces (by pre-set flames applied for precisely equal
[10.3] periods) to a definite viscosity at a particular stage in the machine's cycle must be guaranteed if the products are to be reliable and repeatable. Constant composition of glass and constant properties of the raw stock (thermal capacity, softening point) are important prerequisites here, and it is therefore usually necessary to preselect material before working it. In the case of homogeneity of composition, the glass-working firms

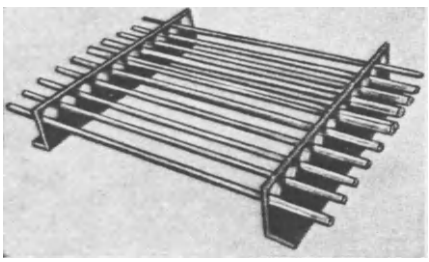


Fig. B 10-116 Device for sorting glass rod and tube by O.D., for use with glass-working machines (made by GLADITZ GmbH)
The two angle sections are slotted with stepwise-increasing gaps; glass rolls over them and drops into the slot which corresponds with the diameter of the rod or tube concerned

used to assume some variation would occur because the glassworks went partly by "home recipes" and would not commit themselves to constant glass composition. However, nowadays a certain amount of standardization and warranty has been achieved, at least by the larger works and foundries.

Quality control and sorting of glass stock for use in glass-working machines. The complexity of exact chemical analysis has generally resulted in determination of expansion characteristics (see 10.2.IV) and viscosity at one or two temperatures (see 10.2.II) as sufficient in practice for ensuring constancy of glass composition; on large-scale production, fitness-for-purpose tests are also carried out, standardized for the job in hand. Large TV tube envelopes, for example, are tested before working both for adequate freedom from strains and for mechanical strength; the latter is tested preferably by hydrostatic external compression with water at 2 atm gauge while the inside is held at 1 atm air (Fig. B 10-5A).

As a rule, it is necessary to size glass tubing or rod for working by machine, and at the same time carefully inspect it if required for air-bubbles, capillaries or chords and striae, which can lead to leaks or electrical break-down in the finished envelope. Pre-sorting of uncut tube or rod by diameter may be carried out in devices like those of Figs. B 10-116 and B 10-116A. Pre-sorted glass tube cut in short lengths, as for making pressed bases (Fig. B 10-134), may often have to be resized since drawn tube does not necessarily have the same diameter over the whole length. (See 10.3.VII for cutting glass tubing.) Automatic sorters are suitable and the working principles of two types are

described in Figs. B 10-117 and B 10-118. In the first, glass tubes drop to various depths, according to diameter, between the conical teeth of a wheel and then as the wheel slowly revolves, are fed into a series of deflectors at different positions with whose help the tubes at a certain depth, i.e. of a certain diameter, are expelled and drop into an appropriate container. In the method illustrated in Fig. B 10-118, two small downward-sloping rollers are provided, one of constant diameter and the other of graded diameter corresponding to the desired sorting. The rollers rotate in opposite directions and their axial separation is adjustable. The rotation of the rollers and their declination produce a gradual downward slip of the components which are fed from a magazine [10.3]

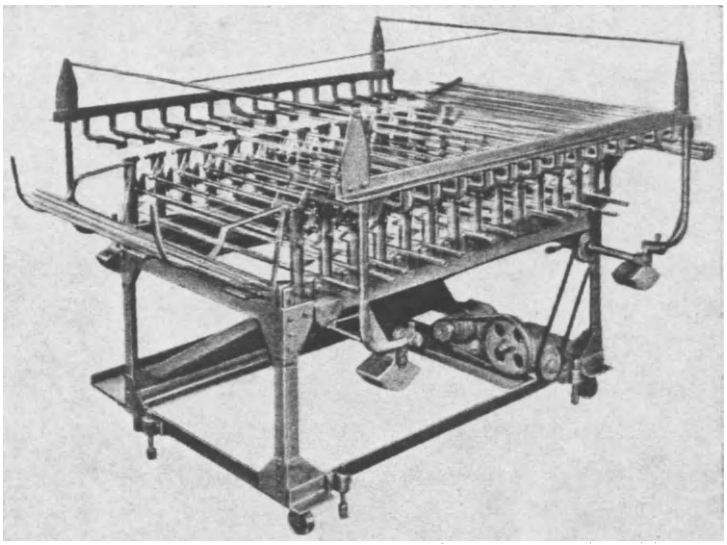


Fig. B 10-116A Automatic glass tube calibrating machine for tube dia. 6–30 mm, and in lengths as supplied by the works
O.D. is measured at both sides of the machine to ± 0.1 mm (type TRS, made by AMBEG, Berlin-Schöneberg)

at the upper end; these components then drop into containers below, through the gap corresponding to their gauge. If still further sorting by inside diameter (I.D.) is required, the parts, cut precisely to length and sorted by outside diameter (O.D.), can then be automatically weighed. Figure B 10-118A shows a fully automatic inspection and sorting machine for cylindrical glass bulbs or envelopes of miniature radio tubes; all the required tests are carried out serially and unsuitable ones are rejected. Such strict selection is only necessary in isolated cases, however. Where small numbers are involved, plug gauges or minimeters are used to measure I.D.

Wall-thickness can be inspected by optical devices especially at places inaccessible or hardly accessible to mechanical gauges, such as the dome of a bulb. The principle is as follows (Fig. B 10-119): the glass under test is placed in the path of a light-beam that has passed through a slit, and which is incident at a known angle α. Part of the beam is reflected at the first surface, part at the second. Both reflected rays are projected on to a screen. From their separation, α, and the refractive index of the glass, one can calculate

the thickness. Figure B 10-120 shows two of these "hollow-ware thickness gauges" for continuous monitoring in the tube factory. The component to be tested is placed on the object stage, which essentially consists of a support with interchangeable annular holders convenient for measuring various sizes and shapes of test-pieces. For small or strongly-curved bodies a cylindrical socket is provided, and a V-block for tubing. Wall-

[10.3]

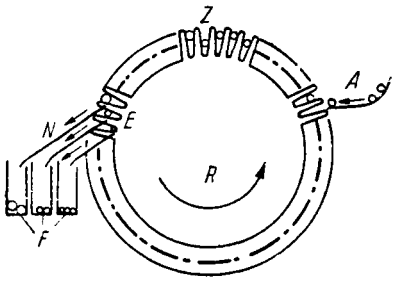


Fig B 10-117 Schematic illustration of a device for precision sorting of cut-off glass cylinders by O.D.

R conical-toothed wheel; *A* feeding components into the teeth; *E* rejection of cylinders by deflectors set at different depths; *F* receptacles into which the sorted tubes fall

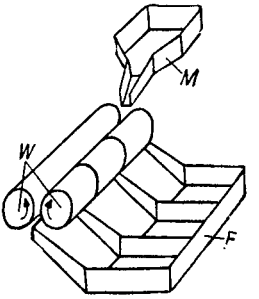


Fig. B 10-118 Precision sorting of tubular glass cut-offs by O.D., using slow-speed rollers

M magazine to take parts to be sorted; *W* stepped rollers; *F* receptacles for sorted tubes

Fig. B 10-118A Fully-automatic sorter for cylindrical glass envelopes of miniature radio tubes (courtesy of GEC-OSRAM, Wembley, England)

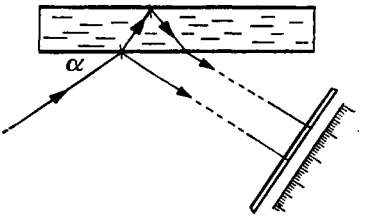


Fig. B 10-119 Ray paths in optical wall-thickness gauge

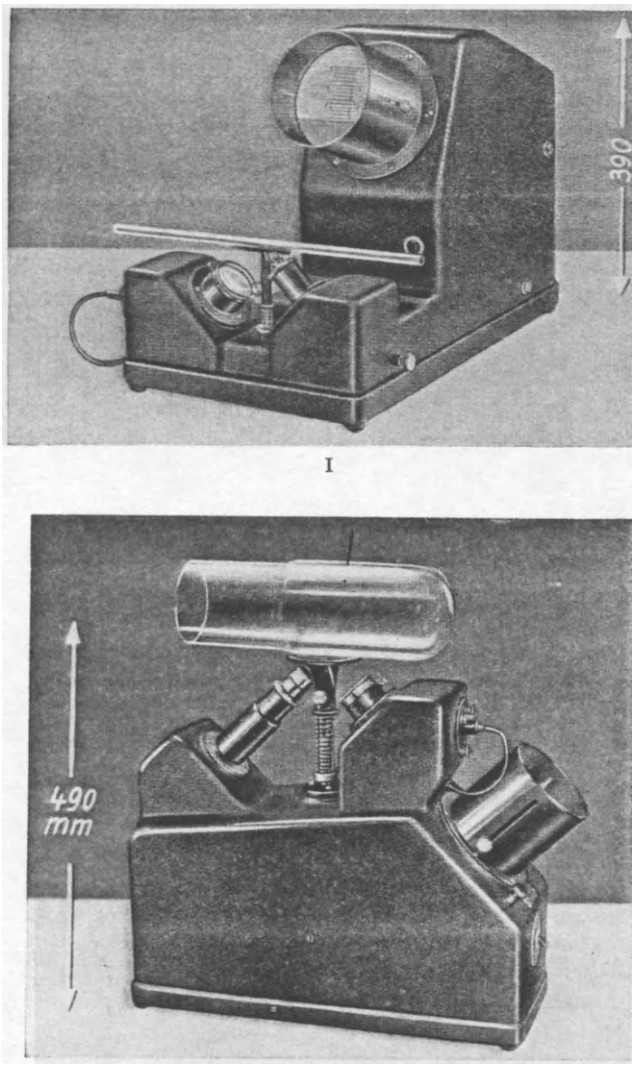
thickness is read directly from the illuminated profile on a ground-glass screen with a calibrated scale (see Fig. B 10-120, III, for a picture of the scale). The range is 3.6 or 10 mm according to model, and the precision is ± 0.1 mm. It may be required to measure laboratory items, to obtain more precise individual measurements, or to gauge larger bulbs and envelopes which must be measured *in situ*, such as glass-envelope Hg rectifiers, or envelopes on the glass lathe. Here it is better to use manual equipment with a micrometer eyepiece which can be placed at the desired area (see Fig. B 10-120A). See Chapter 13, especially Fig. B 13-1, for an optical instrument to measure the thickness of very thin layers of mica, glass and quartz, and transparent plastics, with reliable reading accuracy of $\pm 10\,\mu$, and estimates to $\pm 1\,\mu$. [10.3]

Fig. B 10-119A An optical wall-thickness gauge (courtesy of GEC-OSRAM, Wembley, England)

Figure B 10-120B, I, shows a particularly handy, small wall-thickness gauge. The principle behind it is that if a metal knife-edge is placed near or on a glass surface, a mirror image is seen in the glass wall (ROEPER). Viewed at an angle of 45°, the edge and its image can be seen simultaneously. The distance of the image from the surface is a direct measure of the wall-thickness. Figure B 10-120B, II, shows the details of construction in diagrammatic form. A built-in light source L illuminates the edge S, which rests on the outer wall surface G. The image S' is formed by lens Op at the focal plane of ocular Ok. In this plane lies a graticule with calibrated scale. The image of the edge (SB) and the scale divisions are both in sharp focus as shown schematically in Fig. B 10-120B, III. The scale is calibrated to read directly in wall-thickness. The two edges appear as twin shadows sharply defined; one appears at the scale zero and the second at the scale reading which gives the thickness. If the glass wall varies in thickness then obviously the shadow edges shift along the scale. The whole surface of a test-piece can be examined and the wall gauged at any point without adjustment of the viewer. With this device the wall-thickness of a high-power rectifier envelope can be measured as easily as that of a small lamp.

A far simpler (non-destructive) method which requires no expensive equipment is shown in Fig. B 10-120c; the glass tube is laid on a white paper background and a contrasting (e.g. black) strip of paper is slipped under the tube at an angle. As can be seen from the figure, the outline of the strip is distorted (WITTWER); this outline is observed

[10.3]



I

II

Fig. B 10-120 A commercial wall-thickness gauge with ground-glass screen and scale for continuous monitoring of hollow-ware (made by ROBERT PLAGWITZ, OPT. PRÄZ.-ANSTALT, Berlin-Lankwitz)

I type GD 5 for envelopes up to 150 mm dia. and glass tube of any desired length, scale divisions 0.1 or 0.2 mm, range 3 or 6 mm according to type;

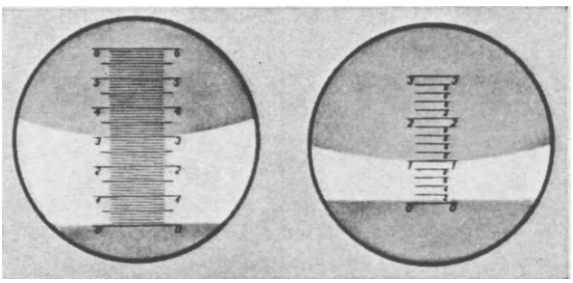
II type GD 2 for almost unlimited envelope diameter, range 6 or 10 mm

through the glass and inspection shows that the distance of the peak of the S-shaped contour from the outer edge of the wall equals the wall-thickness; a rule placed on the tube provides an easy way of determining the distance. The accuracy is sufficient for many purposes, but greater accuracy is obviously obtained by a measuring microscope.

10.3.IIc. *Glass-working Machines, Burner Type*

Those used in high-vacuum work can be divided by type and purpose into four groups:

1. Flaring machines. [10.3]
2. Glass-metal sealing machines.
3. Bulb-sealing machines.
4. Special glass-working machines for preparing and subsequent operations on various devices.



III IV

Fig. B 10-120 A commercial wall-thickness gauge with ground-glass screen and scale for continuous monitoring of hollow-ware (made by ROBERT PLAGWITZ, OPT. PRÄZ.-ANSTALT, Berlin-Lankwitz)

III fine scale; IV coarse scale (120 mm dia.) with examples of measurement. Wall thickness = height of center of white zone

Group 1 comprises all hand-operated semi- or fully-automatic equipment with whose help dishing or flanging can be applied to glass tubing. They are mainly a preparatory stage for the group 2 machines which even today are used primarily to make the classical pinch-foot for filament lamps. Group 2 also contains the machines that make the modern low-capacitance press-foot of electron tubes or at least seal these bases as supplied from the manufacturer to the metal lead-throughs. The bulb-sealing machines of group 3 of the semi- or fully-automatic type seal the pinch with its electrode assembly or the press-foot to the glass or metal envelope which is dropped over. Group 3 also includes horizontal or vertical glass-blowers' lathes which can be used to seal glass to metal rings (see Chapter 30). All other machines, including some very dissimilar types, must be counted as special equipment, in group 4. Examples are: tube-bending, wire-sealing, automatic pumping-stem sealing and bulb-blowing machines, or equipment for making lamp-filament support-hubs with embedded metal hooks. See Section 10.4 for glass-washing machines, bulb-marking devices, and bulb-spraying machines, and Chapter 19 for tube or bulb base machines.

[10.3]

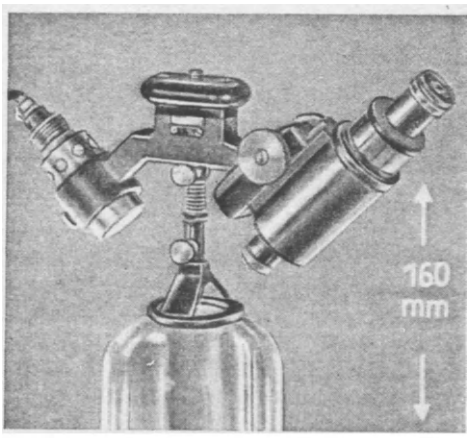
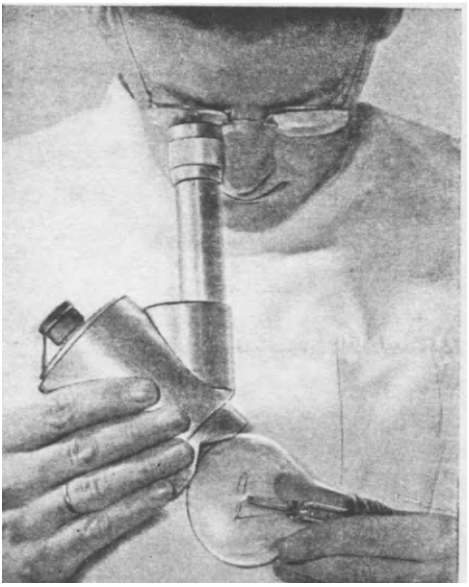


Fig. B 10-120A Measurement of wall-thickness of hollow-ware by micrometer eyepiece for one-off laboratory jobs and for *in situ* gauging of large or built-in devices

Range 10 mm, scale division 0.1 mm (made by R. PLAGWITZ, OPT. PRÄZ.-ANSTALT, Berlin-Lankwitz; type GD 11)



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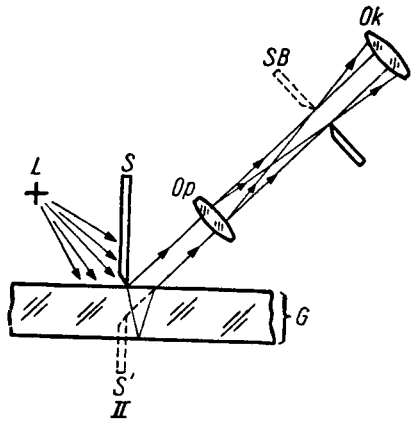


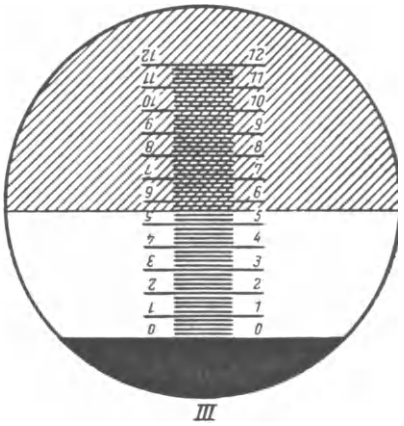


Fig. B 10-120B Small handy optical wall-thickness gauge based on the knife-edge reflexion principle (made by Dr HEINRICH SCHNEIDER, OPTOTECHNISCHE FABRIK, Bad Kreuznach)

I view of the device in use; II principle of measurement (see text); III scale range 10, 3, or 1.2 mm according to type; precision ±0.1, 0.005, or 0.005 mm respectively

1. *Flaring machines.* Flared tubes are one of the most common constructional elements in glass-working (Fig. B 10-125, *h*), being the starting point for all classical pinches. They can be made by flanging the edge of a section of tube with a stationary or counter-rotating flaring- or spinning-tool (Fig. B 10-121). Two U-shaped yokes are arranged one inside the other and the inner one carries the flaring tool. The whole so-called "reamer" turns with the hollow shaft. A second shaft inside the first receives a thrust which imparts a sideways tilt to the inner U-piece and this turns the flaring tool at an angle to the axis *A* as the unit rotates. The mandrel or flaring tool is inserted into the glass tube flame-heated to softening point and forms the edge into a flare. [10.3

Figure B 10-122 shows a simple flaring machine set up for large work. Three chucks are rotated by a central shaft via gear wheels. The operator clamps a cut section of glass in the front chuck after opening the rotating jaws with a foot-operated lever. The

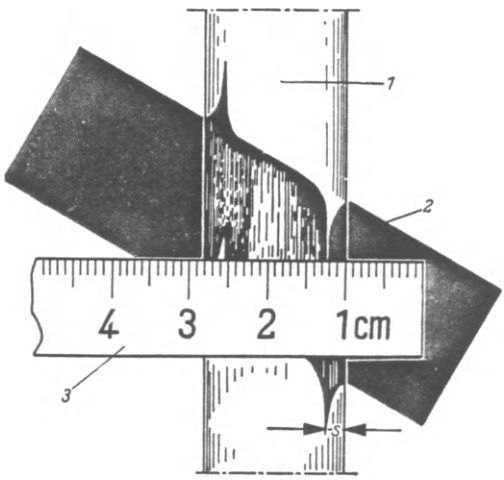


Fig. B 10-120 c Measurement of glass tube wall-thickness (WITTWER)

1 glass tube on white paper background; *2* black paper strip placed at an angle to the tube axis; *3* rule laid on tube to measure wall *s*

hand-wheel is turned a step and the tube is flame-heated at the free end in the second operating position as determined by a notch setting. In the third stage a rotating flaring tool is introduced, carried on a spindle stock whose mechanism was described with the aid of Fig. B 10-121. The flared tube is returned to the original position and extracted after opening the chuck.

Figure B 10-123 shows a fully-automatic flaring machine with eight vertical spindles for smaller jobs. In the upper part of the figure the magazine can be seen; the cut tubes are poured into this, and they drop into the front spindle. Otherwise the mode of operation is as in the large model. It produces about 1000 parts per hour.

A system similar to that of multiple spindle machines in metal-turning can be used instead of the cut tubes, a so-called "off the rod" method (German term). Vertical spindles, 8 or 9 in number, are fed from above with 1–2 m length glass tubes (Fig. B 10-124), and are kept in rotation; a stepped turntable positions each one of the tube ends projecting from its chuck over the various working zones. At the first position the chuck is released and the tube drops on to a stop, whereupon the chuck is retightened.

At the next position the work is gradually flame-heated to temperature and is kept hot until the flare has been formed by the rotating reamer from below. At the last position, the desired length is cut off the tube. The flared tube slides down a chute to a tempering oven with a traveling grate and is completely annealed by the time it leaves the grate. These fully-automatic machines make about 1000 flares an hour or more.

[10.3]

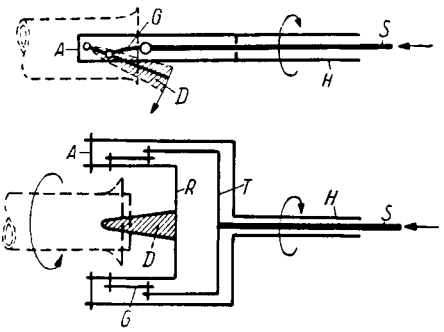


Fig. B 10-121 Diagram of operation of a flaring tool (reamer) for glass tube (stem)

S rod in hollow shaft *H* supported to allow sliding; *T* outer U-piece; *G* link; *R* inner U with reamer *D*. While the reamer rotates against the work (dashed line), *S* is forced to the left so that *R* and *D* swivel

The completed flares are often "spread" before working into pinches, that is, the end opposite the flare is stretched into a bowl shape by means of expanding jaws (Fig. B 10-125, *a–c*). The spreader machine has a turntable on which the flare moves from one flame to another in steps which heats it more at each step until at the proper position it is spread by the cam-operated jaws.

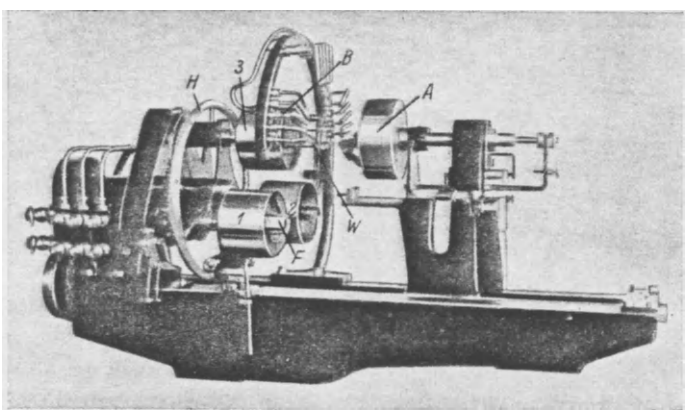


Fig. B 10-122 Large flaring machine, made by SCHMIDT UND KLEINBERG GmbH

F chuck; *H* hand-wheel for stepping the 3 rotating chucks; *B* burners for heating work *W* (in position 3) at the face of the rotating reamer *A*

2. *Glass-metal sealing machines.* One of the hardest glass-working jobs is making reliable seals between glass and metal for vacuum use and for glass technology. Therefore, the technique has a special chapter devoted to it (Chapter 30), subdivided by metals suitable for glass sealing; not only has the glass type to be chosen correctly, but also the best metal to use, and its shape and treatment. Only those machines and devices which are suited to *all* correctly chosen glass-metal pairs are dealt with here.

Vertical pinch-feet. The classical pinch-foot still plays an important part in vacuum technology, especially in ordinary filament-lamp manufacture; its construction is shown schematically in Fig. B 10-125. The pinch process proper is combined with insertion of the pumping stem for the feet of a series of tube types (large radio tubes, standard filament lamps). Details of manufacture will be given below with the description of mechanical equipment.

Very large pinch-feet are not produced in large numbers and are therefore made as one-off jobs by stem-pressing jaws (Fig. B 10-126). The pre-spread flare is clamped in a bridge and the metal lead-throughs rest in an anvil (cf. Fig. B 10-129). (In many [10.3]

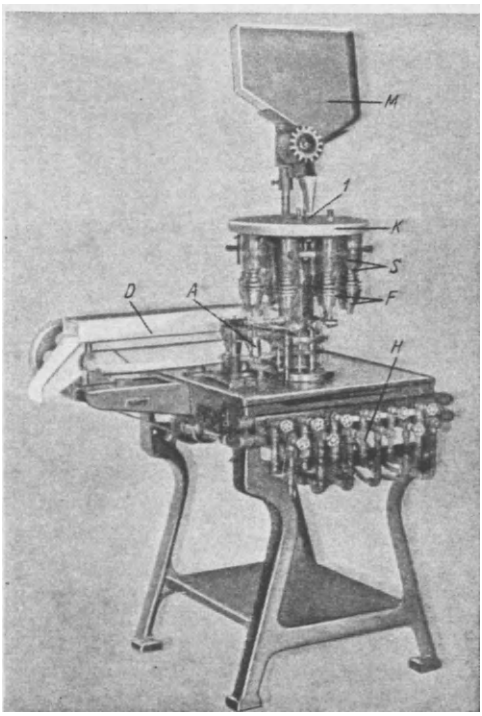


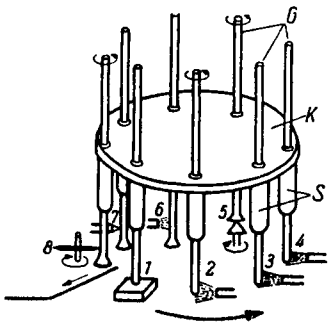
Fig. B 10-123 Eight-spindle automatic flaring machine (made by GLADITZ GmbH). Output 1000 parts/hr

M magazine for cut sections of tube; *K* stepping turntable; *S* spindles with chucks *F* into each of which at the first position a section of tube drops; *A* reamer; *H* taps for controlling burner feed; *D* asbestos-clad annealing lever

cases, e.g. large tubes with thick lead-through rods, the rods are glass-wrapped over the sealing length before pinching and the wrapping made vacuum-tight by torching; in this way the actual pinch seal is made between the sheathing glass on the rods and the glass of the flared tube.) The rod-spacing is set by the holes in the anvil. Either side of the flare tube are burners to heat the spread tube foot and the metal leads, and arranged as desired on a circle of holes or set on a rotatable ring. To heat the area of interest, the burners and hole-ring can be raised or lowered by hand-wheel *D* or foot-lever, or if the burners are fixed, the work can be shifted. When the glass has reached the correct temperature for sealing, the press jaws *Z* are operated by a lever and the pinch is formed. As the foot is being made a slide bar *S* comes up, guided by a hollow shaft, and smooths the glass surface between the pinched wires, or it may impress

surface hollows to increase the area, and hence the surface resistance between the leads by lengthening the leakage current path. To clamp the flare tube, spring-loaded jaws of prismatic cross-section or spring-loaded brass cheeks in guides are provided. In special cases the pressing jaws are also arranged in horizontal guides somewhat as in Fig. B 10-126, II; in fact, the construction of glass-working machines is very variable and only examples can be given here. The material for parts that form glass, such as the silde bar and pressing jaws, is generally oxidation-resistant brass or CrFeNi alloy.

[10.3]



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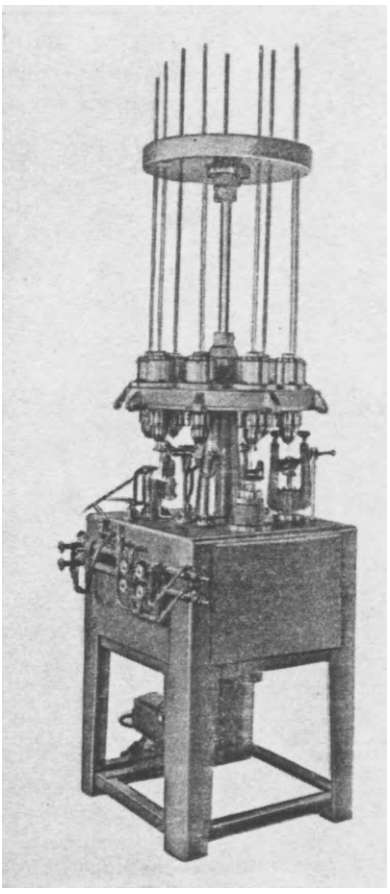


II

Fig. B 10-124 Automatic flaring machine working "off the rod"

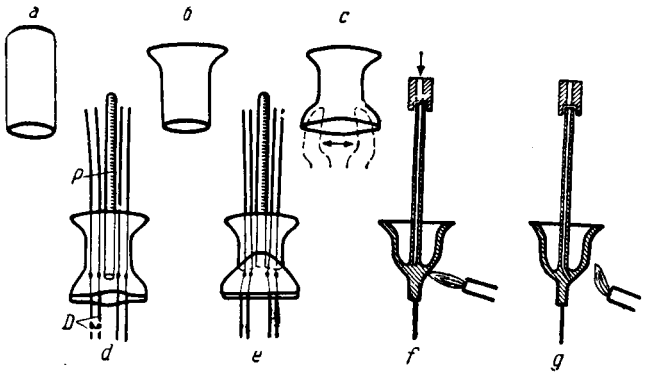
I diagram of construction: *K* stepping table; *S* rotating spindles with glass tubes *G*. Working cycle: *1* limit stop and chucking; *2–4* heating lower end of tube; *5* flaring with reamer; *6–7* heating cut-off area; *8* cutting flare section from tube with rotary, cooled carbide slitting disk

II Specifications: for flares with 6–14 mm dia. or 14–21 mm dia., 15–50 mm long, 1000/hr (type TEL 9, made by G. BRÜCKNER, MASCHINEN-FABRIK, Coburg-Neuses, and SCHMIDT UND KLEINBERG GmbH, Neu-Ulm/Donau)

Similar in construction to the semi-automatic large-pinch machine is the universal machine for working small one-off parts (Fig. B 10-127); its chief use is for laboratory work and non-repetitive jobs. Replacement of the stem-pressing jaws shown in II of the figure enables the machine to do other work such as flaring (see III) or bulb-sealing (see IV).

The mass-production stem-pressing machines only differ from these one-off units in the number of working-points and hence in the amount they can produce. For instance,

Fig. B 10-128 shows a 12-position, fully-automatic stem-pressing machine where jaws of the type in Fig. B 10-128A are arranged on a turntable. Besides those for ordinary flat pinches, there are jaws for cross-pinches (Fig. B 10-128B) and the so-called "profile



[10.3]

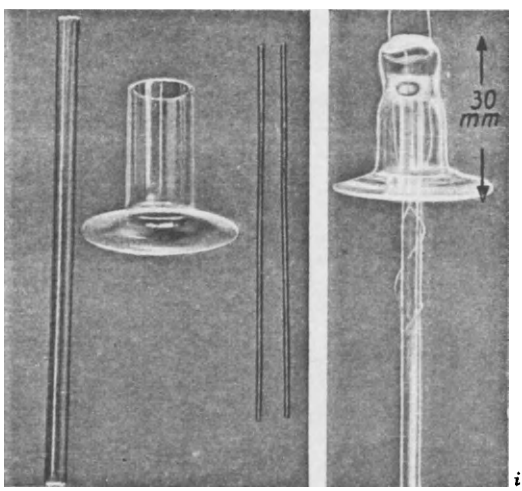


Fig. B 10-125 Preparation of a pinch-foot

a–c spreading the flared tube; *d* insertion of lead-wires *D* and pumping stem *P*; *e* making the pinch; *f–g* blowing a hole in the wall to the pumping stem; compressed air blown from the top end of the stem forces through the part of the glass softened by the pointed flame. Lower illustration (photograph): *h* pumping stem, flare and lead-wires before sealing; *i* completed pinch of a luminescent lamp with low-pressure Hg discharge filling as in Fig. B 10-231

pinch". Figure B 10-128C shows examples of profile pinches. The burners are fixed and stepwise travel of the work from position to position may be either foot-operated or fully-automatic.

One can distinguish here two fundamentally different types of machine by the mechanism of the stem-press. The first type (Fig. B 10-128) has pinch jaws which turn with the work, that is, each set of jaws moves with it from one position to another, and at

the appropriate moment are operated by a cam-driven rod that lies in the hollow drive shaft, without rotation of the pinch-foot carrier being interrupted. These machines with rotating sets of holders often have the advantage of easier interchange of jaws for pressing, and other work such as bulb-sealing (see below) can be undertaken on the same machine without a tedious conversion process. The second type contrasts with the first in that the holders for sealing-wires and the flare piece do not turn during rotation of the table, and only one or two fixed-position jaws are arranged along the periphery of the turntable; the flared tubes for pinching are then fed through these jaws. The pro-
[10.3] cess is somewhat as follows: as before, the work is gradually heated as it passes through

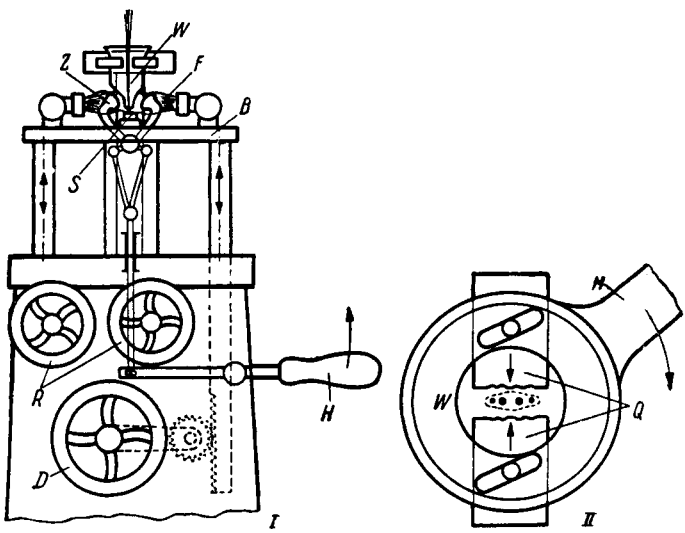


Fig. B 10-126 Equipment for stem-pressing

I machine with hinged jaws: *W* work (flared tube); *S* anvil to hold pinch-wires and smoothing rod; *F* flames from burner on bridge *B*, adjustable for height by hand-wheel *D*; *Z* pinching jaws operated by a control rod from lever *H*; *R* hand-wheels for gas and air inlet control. II example of drive for operation of pinch-jaws in guides: *W* work (prespread flare tube). The jaws *Q* are propelled in the direction of the arrows by lever *H*

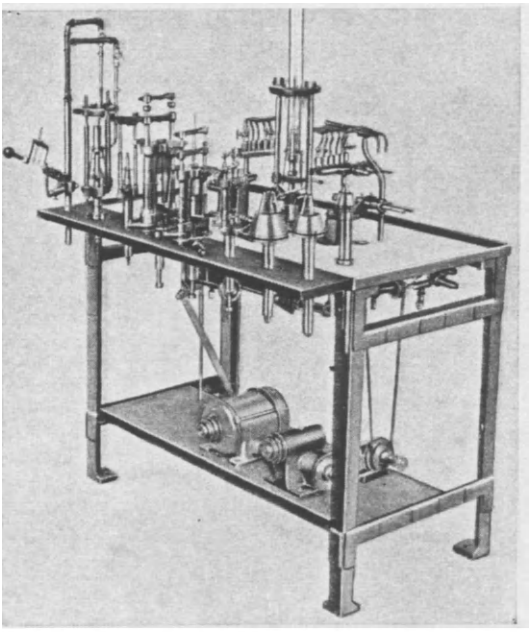
groups of flames at various positions. By the time the work reaches the first pressing tool it is so soft that it is in danger of flow deformation, so the first tool gives the glass a certain degree of pre-pressing. A short heating follows as the table moves on, and finally in the position of the second stem-pressing tool the pinch is completed. Figure B 10-126 illustrates the kind of operation which occurs with these fixed-position cam-operated jaws.

As already mentioned, in most pinches the exhaust stem is sealed in with the lead-wires on the stem-pressing machine (tipless tubes, see Fig. B 10-125, *d*, *e*, *h*, *i*). However, the opening of the stem is closed in the pinch process and must therefore be reopened, as in Fig. B 10-125, *f* and *g*. A pencil flame is used to heat the area where the hole should be so that compressed air blown into the glass tube forms a convex bubble on the outside. The bubble bursts and the hole is thus formed. The outgoing stream of air blows the flame to one side and avoids further heating of the glass.

There is a wide variety of devices to drive the turntable and the holders with rotating stem-pressing jaws. A common one for the table drive is a Maltese cross (Fig.B 10-129) which sits on the table and is stepped by a driving plate turned by a change gear or worm gear and friction coupling or dog-clutch from an electric motor. Gears make it possible to have different working speeds. The output can amount to 100–500 parts per hour.

Generally, these machines have one operator. However, the large demand for general-purpose lamps of 15–100 watts (see, e.g., Fig. B 3.2-23) has led to the manufacture of complex, fully-automatic machines which do not only pinch pre-flared tubes and provide them with exhaust stems and central glass rods (hubs) for assembly of filaments, but also seal the Mo wires that carry the W coils into the glass rod (Fig. B 10-146). Fig. B 10-130 shows such a machine with 28 positions and a glass consumption of *ca.* 3 m^3/hr at 1 kW input power; its output of complete 100 W lamp-stems is up to 1250 per hour. Obviously, all component feeds are fully-automatic and so is the throughput of finished stems via a slipway to the traveling grate of the associated tempering oven where the stems are forthwith annealed. (See 10.3.VIII.)

Horizontal flat pressed bases. In the construction of small amplifier tubes, there has been an increasing tendency since the start of World War II to replace the classical pinch-foot by flat or dished pressings (cf. Fig. B 10-131). This permits a considerable decrease in tube height as well as lower capacitance loss across the lead-wires, longer insulating glass path be-



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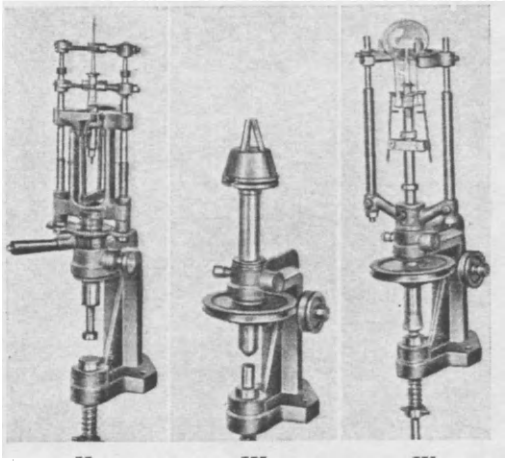


II III IV

Fig. B 10-127 Universal machine for semi-automatic glass-working (made by GLADITZ, Schwäbisch Gmünd, Württemberg)

I rear view with table for various processes: changing the holders gives a choice of stem-pressing with holder II, flaring with holder III or bulb-sealing with holder IV

[10.3]

tween leads, and also greater mechanical stability of electrode assembly; the latter is primarily due to the non-planar array of leads in contrast to the standard vertical pinch arrangement. Figure B 10-132 compares earlier and modern radio tubes, and the advantages of the modern system are obvious. When required, an astonishing number of pins can be fed through a very small base, as shown in Fig. B 10-132A, where a special tube of 42 mm height has no fewer than 27.

[10.3]

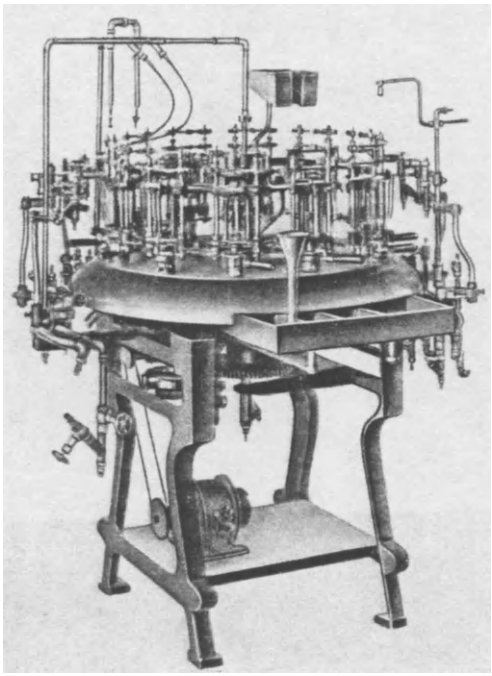


Fig. B 10-128 Fully-automatic stem-pressing machine with 12 holders (made by GLADITZ GmbH)

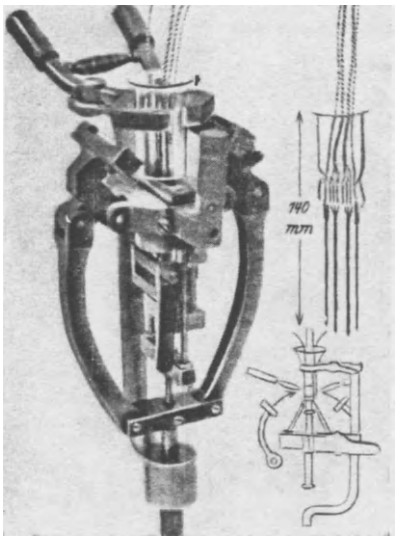


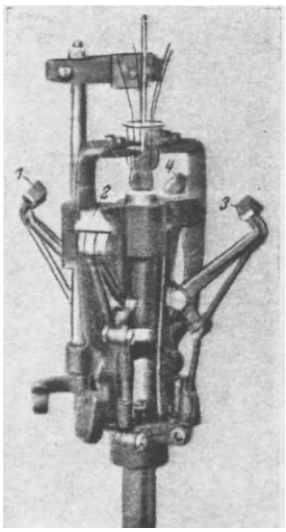
Fig. B 10-128A Stem-pressing or pinch-holder, with sealing-wires and flared tube (cf. [1]EISLER)

Lower right: schematic; upper right: completed pinch-foot

Manufacture of small flat and dished presses for radio receiver and amplifier tubes is carried out on automatic turntable machines by various methods of which the following have proved successful in quantity production:

(a) *Glass bead method* (Fig. B 10-133). Wires or pins are placed either by hand or automatically in holes arranged in a die plate and over each is dropped a loose-fitting glass sleeve; for exhaust-stem presses, a small suitably shaped pumping tube is dropped in a central hole in the plate (Fig. B 10-133, *a*). As the plate rotates, the glass sleeves are heated to a softness at which they will just flow and seal to the lead-pins. After renewed heating, in the next position of the turntable, a plunger (top die) with holes to take the upper lead-ends presses downwards on the glass mass to form it to a flat disk and joins it to the flanged top of the exhaust stem; the pins which are now sealed vacuum-tight are held vertically in the disk.

(b) *Glass ring method* (Fig. B 10-134). Another method is to use two concentric glass rings cut to appropriate lengths, in place of the sleeves of the previous set-up. Figure B 10-134A shows an automatic machine for making press-feet and the devices that feed the die with lead-through pins and rings (corresponding to Fig. B 10-134). For miniature tubes (Fig. B 10-132, III) with bases of about 15–20 mm dia. without pumping stems, the inner ring (Fig. B 10-134, 2) can be omitted and the outer one alone provides the glass to make the press-foot. Figure B 10-134B shows a machine for these miniature [10.3]



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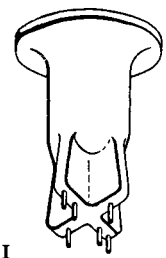


II

Fig. B 10-128B Stem-pressing holder for cross-pinches (made by EISLER ENG. CO.)
I, *1–4*: pinch jaws; II completed pinch

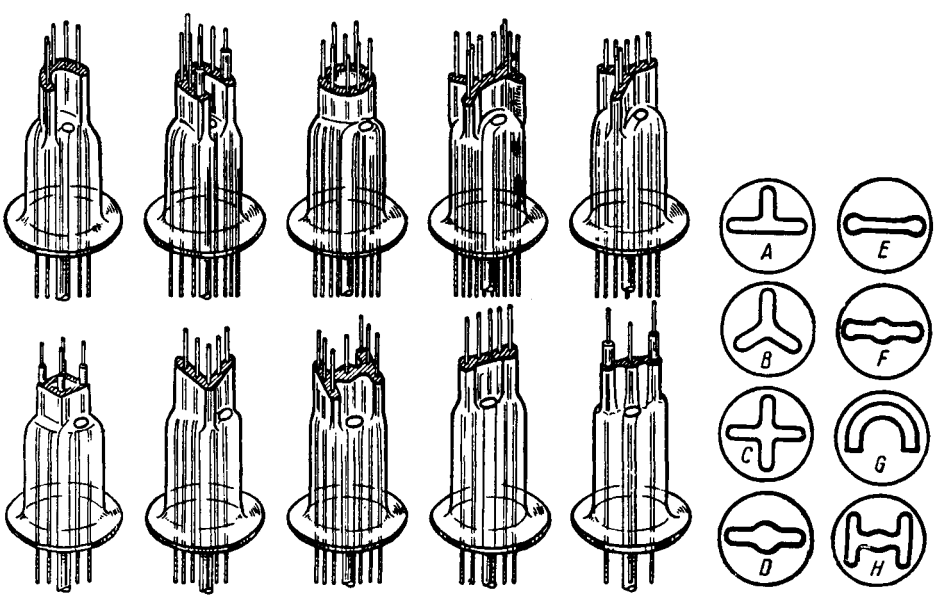


Fig. B 10-128C Examples of profile pinches; perspective and cross-sections (collection by [2]EISLER)

[10.3]

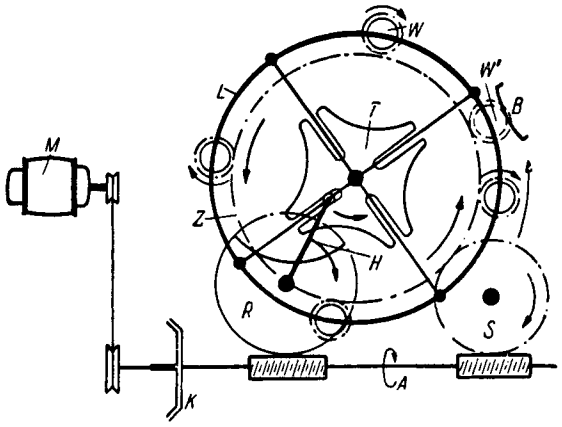


Fig. B 10-129 Simplified operational diagram of 4-position pinch- or wire-sealing machine

Motor *M* and clutch *K* turn shaft *A* and its two worm-gears. Four stem-holders *W* are fixed to turntable ring *L* and are driven by the large toothed wheel *Z* via worm-drive *S*. Gear *R* is connected with link-arm *H* which steps the Maltese cross *T* and ring *L*. Holder *W'* with the completed work pauses at *B* (position *1*), as a brake is applied to a friction clutch, so that a new piece-part can be installed

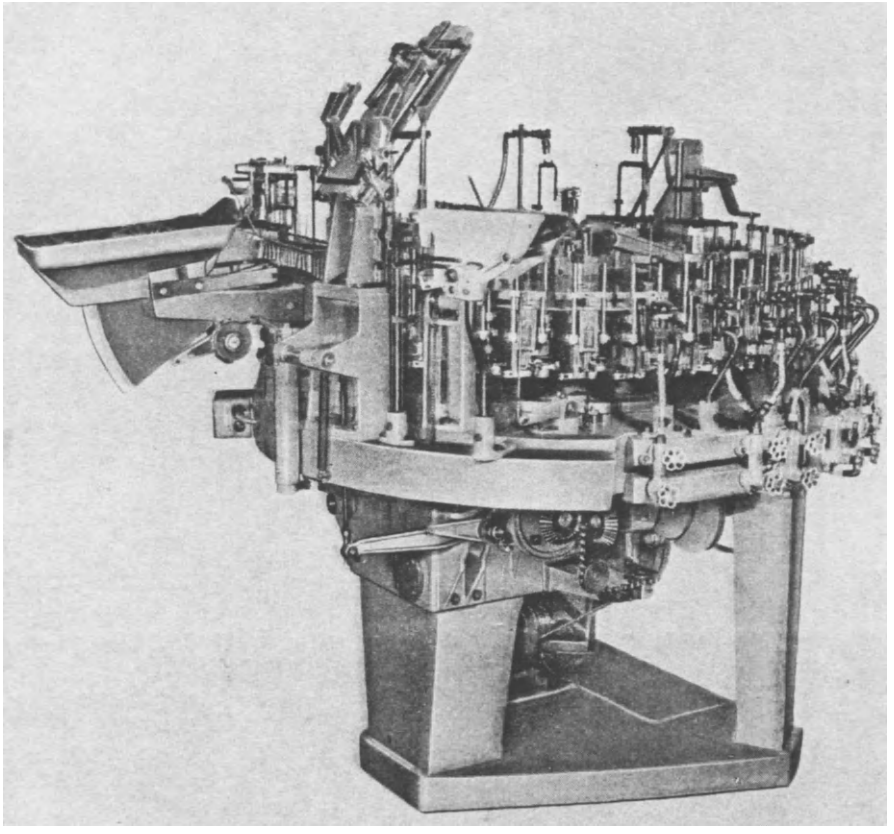


Fig. B 10-130 Fully-automatic stem-pressing machine for tungsten filament lamps (15–100 W, general-purpose type)

This machine makes vertical pinches with pumping stems and central filament-support glass hub (22–60mm long); it also embeds Mo wires (without hook ends) in the rod to hold the W filament coils. Output up to 1250/hr (type F 600; made by G. BRÜCKNER, MASCHINEN-FABRIK, Coburg-Neuses)

tube press-feet. In the case of flat bases for so-called "all-metal tubes" with glass bottoms, used for a long time in USA, and Europe also, for radio tube construction, the bottom mold has an additional outer ring of metal; this ring is sealed vacuum-tight with the press-foot at its outer edge by melting the glass ring and pressing, in the same way as the leads are sealed to the glass. Figure B 10-135 shows the sequence of operations.

According to the construction of the electrode system on the pressed flat base, the metal envelope is joined to the outer rim of the flange of the metal base-ring by seam [10.3]

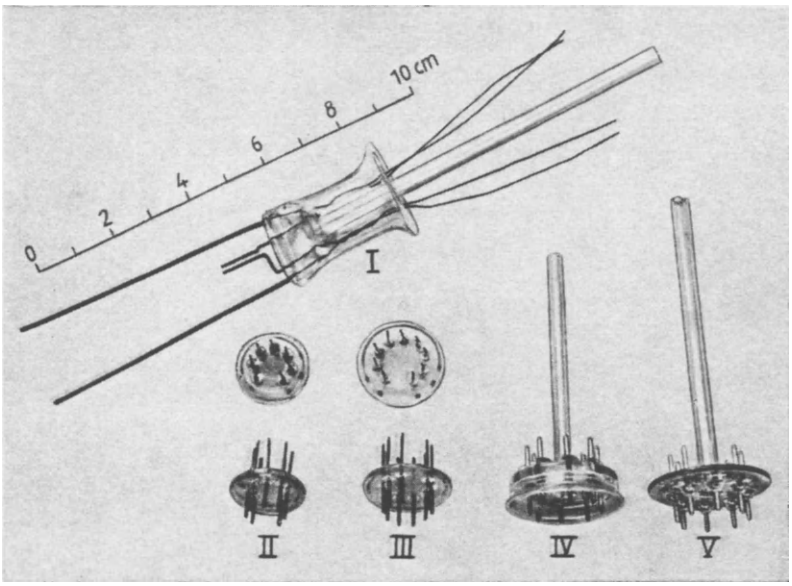


Fig. B 10-131 Press-foot (flat) and dished foot-bases compared with the classical pinch-foot

I vertical pinch for large triode
II flat pressed base 16 mm dia., 7 Dumet leads
III flat pressed base 23 mm dia., 9 Dumet leads
IV dished base 30 mm dia., with exhaust stem and 8 CrFe leads
V flat base 31 mm dia., with stem and 8 CrFe leads

or edge (resistance) welding, to make a vacuum-tight seal. To facilitate this, the base-ring is often made in two sections, an inner glass-sealing ring of ferritic CrFe and an outer one of Zn-plated sheet Fe. Such tubes were made in the years shortly before World War II by RCA, and later in improved form by TELEFUNKEN, on a mass-production scale, and were known as "all-metal" tubes; on efficiency and technological grounds (degassing the metal envelope, difficulty in gettering, poor radiation cooling of the electrodes) they proved uneconomic in the long run, and were replaced by flat-base "all-glass" tubes.

(c) *Glass-drop method* (see Fig. B 10-136). Here the glass for the base is not introduced as a piece-part in solid form which is first heated in the bottom die, but is presented as a blob of viscous fluid taken directly from the furnace. This is the preferred method therefore for firms which make their own glass in a tank furnace.

[10.3]

Fig. B 10-132 Comparison of sizes of radio tubes with vertical pinch-feet and horizontal press-feet; (a) photograph, (b) corresponding X-ray photograph (²KRATOCHVÍL)
I diode rectifier VALVO AZ 11; dia. 37 mm, height 110 mm including plastic tube-base
II miniature H.F. triode SYLVANIA 12 AU 7; dia. 22 mm, height 55 mm, with 9 CrFe pins (cf. also Fig. B 5.2-14)
III subminiature tube PHILIPS DL 71; dia. 9.7, height 38 mm, 5 pins

(d) *Cast-glass dished presses.* It is an advantage when making transmitter tubes (see, e.g., Figs. B 5.4-15, B 5.4-17, B 5.4-17c) to draw the large and correspondingly thick-walled pressed bases ready-made from the works as semi-finished products with impressed tubular lugs for the lead-throughs. It should be noted here that as a rule pressed

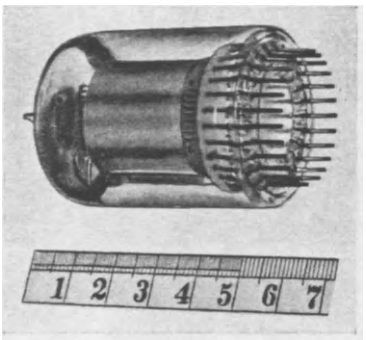


Fig. B 10-132A Press-foot tube with 27 current pins on a 28 mm pitch circle; diameter of base (Pb-glass) 42 mm. Storage tube designed by UHLMANN for telephone system; has I.H. oxide cathode, 1 anode and 20 secondary emission electrodes (courtesy of ERICSSON) [10.3]

glass requires thicker walls than blown glass so that the glass remains fluid enough to fill the whole mold. These bases should come plane-ground and polished, if possible, on the outer rim and at the edges of the openings for lead-wires (e.g. Fig. B 10-137). If polishing is omitted and rough-ground edges are accepted as satisfactory, the joint to

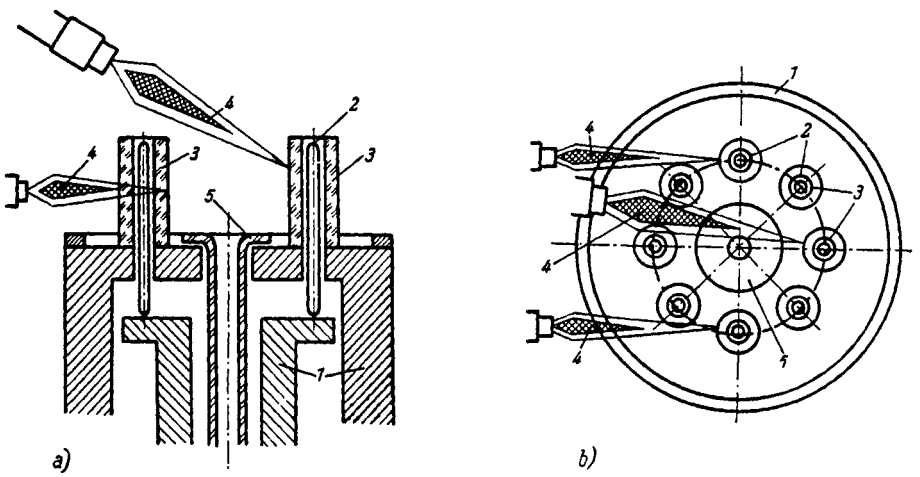


Fig. B 10-133 Manufacture of flat press-foot with exhaust stem by the bead method ([1]KRATOCHVÍL VIOLET)

(a) cross-section, (b) plan view, at start of automatic sealing process. *1* rotary die plate; *2* sealing wire or pin (e.g. CrFe); *3* Pb-glass drop-over sleeve; *4* sealing flame; *5* preformed pumping stem (Pb-glass). After melting, the whole viscous glass mass (plus flange of pumping stem) are pressed by a flat-ended perforated top-die to form a single disk (Fig. B 10-131, V)

the envelope and lead-wire sheathing clearly shows up as a "seedy" zone (due to fine bubbles); if the edges are polished, the sealing zone remains clear. These bases are usually provided by the tube manufacturer with a pumping stem and pre-glassed Kovar, FeNi or Cu caps in a single operation on one-position vertical rotary machines

(Fig. B 10-137, III). When the assembly has been mounted on a horizontal glass-working lathe (Fig. B 10-144), it is sealed to the envelope (Fig. B 10-145). See Chapter 30 for direct manufacture of cast-glass to metal seals.

3. *Bulb-sealing machines.* These are for joining the edge of the pinch or pressed base to the envelope after the electrode assembly has been mounted on the base.

Methods. In filament lamp and amplifier tube manufacture, where vertical pinches are employed, the process approximates to that shown schematically in Fig. B 10-138. The machine holders with foot and envelope rotate continuously. The envelope is first

[10.3]

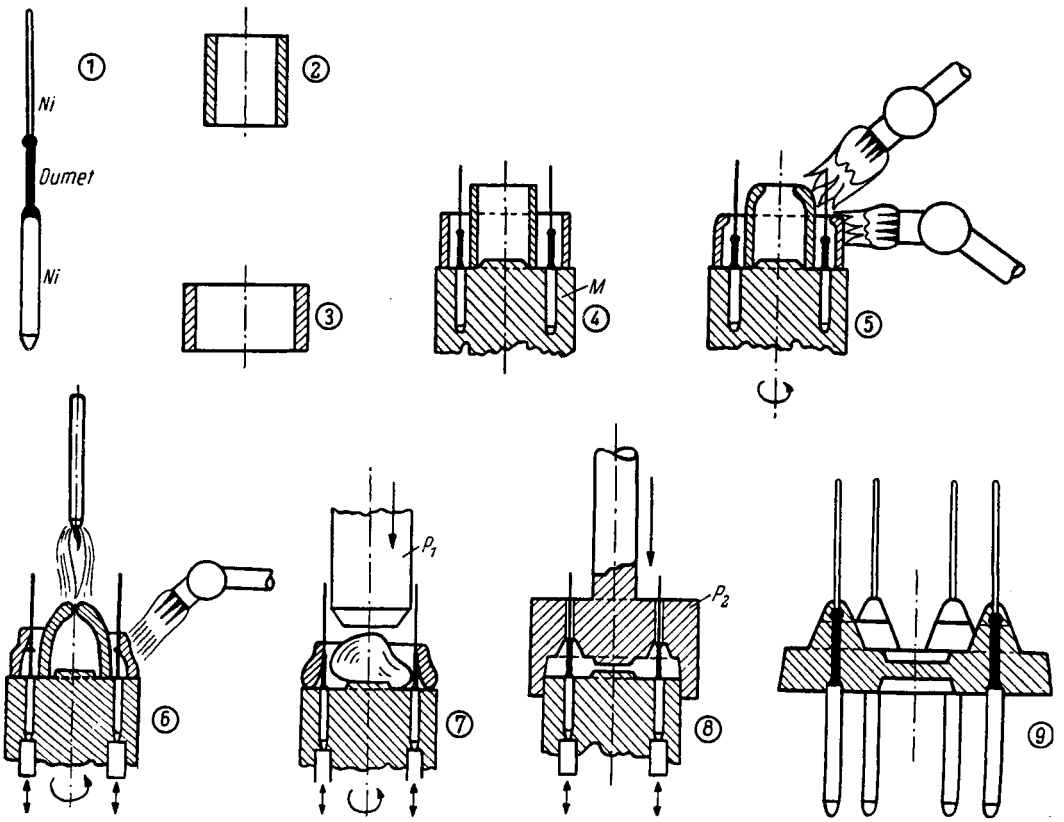
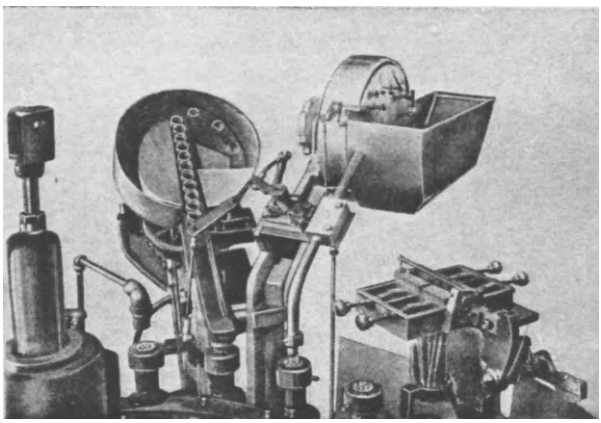


Fig. B 10-134 Concentric glass ring method of making flat presses (MILLNER)

1 3-section sealing pin of Ni and Dumet (see 6.5.IX), welded; *2* inner ring of glass (may be omitted on miniature tubes, dia. 15–23 mm); *3* outer glass ring; *4* bottom die *M*, with components, lasts *5–6* sealing operations; *7* prepressing with top die P_1; *8* final press with P_2; *9* completed base stem

warmed with a brush flame, and as heating proceeds near the flared tube, the glass softens to the point where it "necks"; this is partly due to the pressure of the flame, partly from the weight of the skirt below the rim of the base, which primarily causes reduction in the diameter of the neck of the envelope and then reduction of wall-thick-



[10.3]

Fig. B 10-134A Partial view of 24-position fully-automatic machine for making flat press bases with 8 CrFe lead-pins and exhaust stems

Right front: magazine for pins; upper middle: bucket drum for placing inner glass rings; upper left: cartridge drum for placing outer rings (made by KAHLE ENG. Co., North Bergen, N.J., USA)

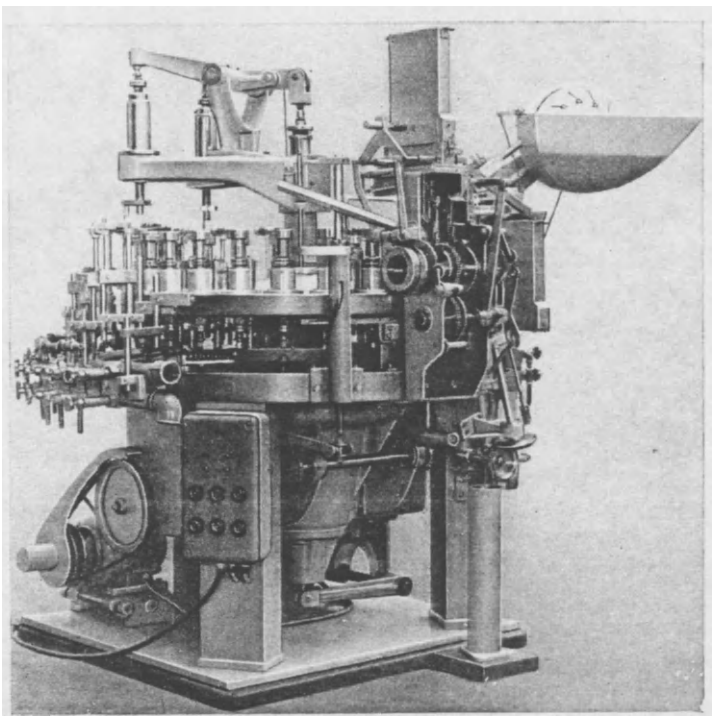


Fig. B 10-134B Semi-automatic 24-position machine for making press-feet of miniature tubes (made by ELSTROJ-Prague, type 2 S)

Output: 350–700/hr depending on size

ness at the hot zone. After mating the base edge and the envelope and sealing thereof, the overhang of the latter is cut off by a pointed flame. It is a natural proviso that the shape, viscosity and expansion coefficients of the coincident glasses match each other to produce a reliable joint. Soft-glass tubes usually have 30% lead-glass for the foot, and

[10.3]

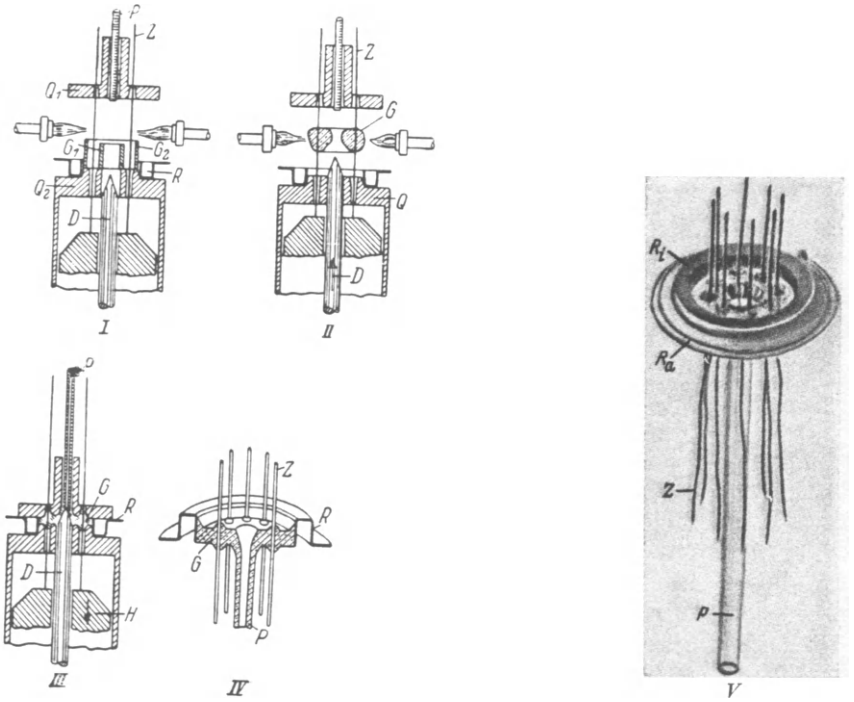


Fig. B 10-135 Manufacturing process for a press glass foot for metal-envelope tube (⁵ESPE)

I set-up at start of sealing operations; Q_1 and Q_2 top and bottom die, G_1 and G_2 inner and outer glass rings, Z lead-wires, R flanged metal ring, P pumping stem, D mandrel

II glass is sealed to wires (G to Z), mandrel D is raised, G is reheated and the press process itself then follows:

III as the glass is pressed into ring R, mandrel D keeps the pumping stem open

IV cross-section of finished base

V view of finished base; in this construction ring R is in two parts, an inner sealing ring R_i of CrFe and an outer R_a of Zn-plated sheet-Fe

magnesia glass for the envelope (see Table T 10–4 and corresponding parts of Table T 10–2).

The shape of the "neck" after seal-off of the envelope is important for a firm fit of the base socket, which is cemented on afterwards. It is often not regarded as sufficient to rely on the "natural" shape of the necking after the collapse of the envelope, so auxiliary formers may be used. By impressing channels, the "form-lock" of the subsequent cementing process can be ensured.

Sealing the envelope to the press-foot or dished base is somewhat different from the pinch process (Fig. B 10-139). Proximity of glass-metal seals and electrode assembly prohibits as large a working flame or as broad a heating zone on the envelope. The

envelope is therefore cut to length and is arranged on the automatic machine without any overhang relative to the foot so that the rims of envelope and foot lie close together. In contrast to lamp-bulb sealing, the envelope is offered from below so as to avoid, as far as possible, rising hot air and flame gas from reaching the electrodes. It is best to work with pointed flames of oxyhydrogen gas instead of city gas; this is because first, the flame can be kept smaller for the same heat-production and sealing is quicker with-

[10.3]

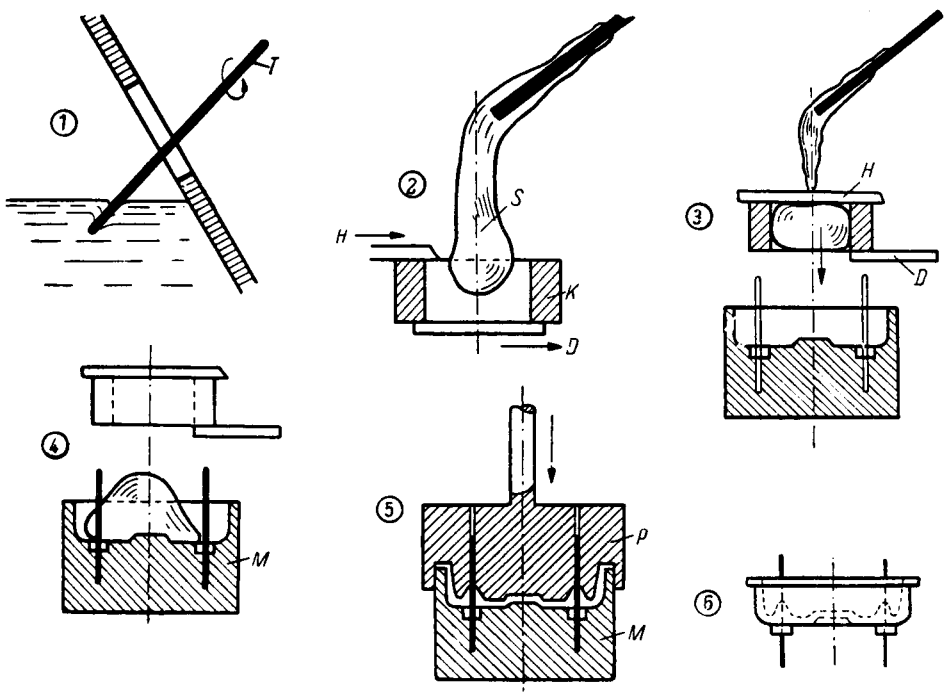


Fig. B 10-136 Manufacture of pressed glass foot from a fixed amount of molten glass (MILLNER)

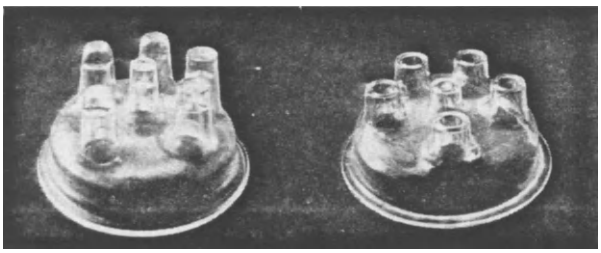
1 take-up of glass gather from furnace with a rotating dip-stick; *2* dropping glass *S* into dosing chamber *K*; *3* closing top of chamber *H* after filling and cutting off excess glass and simultaneous opening of lower end by withdrawal of cover *D*; *4* viscous glass dropped into bottom die *M* which contains sealing wires; *5* pressing dished base with top die *P*; *6* completed base and leads

out overheating the electrodes, and secondly, the sulfur content of city gas may reduce emission from oxide cathodes by BaS formation.

Dry air at low pressure is often blown over the electrode assembly to cool it during the sealing process; it also prevents too much collapse or constriction of the glass in the hot zone, or it may be used to round-off ("radius") the seal area. If there are sensitive materials such as Zr coatings in the tube, or if the distance between the sealing zone and electrode system is short, it is recommended that while sealing proceeds a flushing gas be used; this should be dry, oil-free N_2 fed in by a sleeve slipped into the pumping stem as in Fig. B 9.2-20. If the tube is sensitive, flushing gas at reduced flow-rate should be introduced during the subsequent tempering process until the tube is cooled to a

temperature at which oxidation of the relevant parts and appreciable gas-absorption need not be feared. A more effective way of keeping the electrodes cool and avoiding cathode poisoning is the one shown in Fig. B 10-139A for joining envelope to pressed

[10.3]



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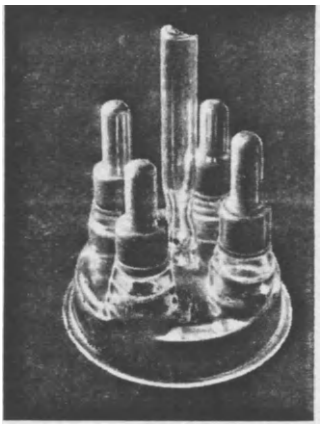

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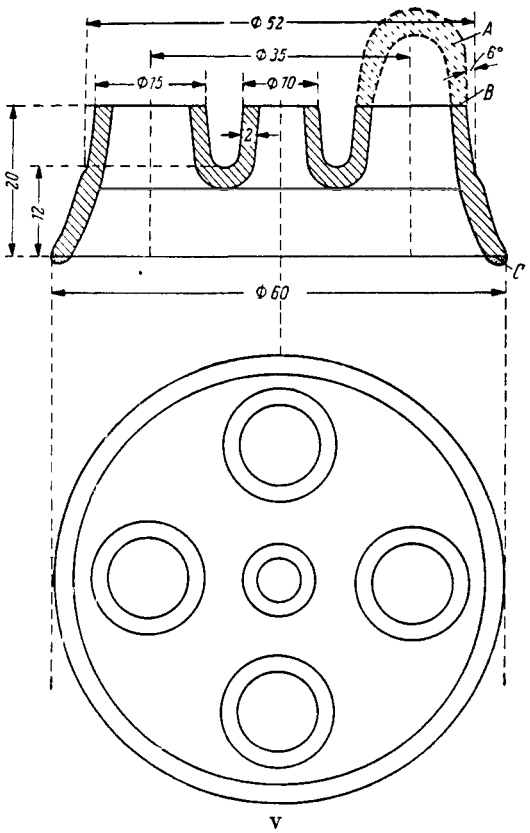


IV V

Fig. B 10-137 Dished glass feet as supplied from glassworks, for making transmitter tubes of type in Figs. B 5.4-15 or B 5.4-17 c

I as taken from the mold, ends of tubular lugs still sealed over; II ends ground off; III pumping stem and metal caps sealed on; IV example of dimensions, in cross-section (hatched portion *A* is before grinding-off; *B* and *C* are polished edges after grinding-off); V plan view of IV

base. The rotating envelope and base edges are held apart and heated and softened by H_2—O_2 flame while the electrodes are cooled by a stream of dry air; at the last moment, the two edges for sealing are mated by rapidly lowering the electrodes into the envelope,

and then fused together. Naturally, this method is not possible for tubes with no free-standing electrode system, but where the electrodes are held against the envelope wall by saw-edged mica disks or leaf springs.

An excellent method of protecting the electrodes from hot gases is optically to polish the sealing edges of base and envelope, mount the assembly on the press and then bring both edges into contact; the tube is then evacuated and atmospheric pressure forces the edges together to make a fairly vacuum-tight joint. To produce a final seal it is enough to heat the seam and its surroundings to a temperature well below the deformation point M_g (see Table T 10–5) with a S-free butane-propane flame. Another way is to [10.3] heat the assembled tube (Fig. B 10-139B) in an ordinary electrically heated hood-oven

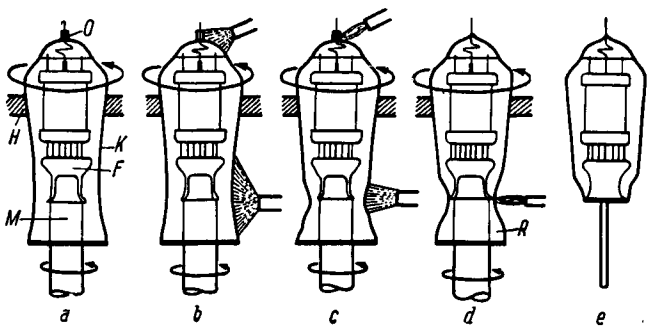


Fig. B 10-138 Sealing envelope to vertical pinch

a foot *F* is set in the machine holder *M* and envelope *K* dropped over; *H* is holder for *K*;
b preheating *K* in brush flame;
c *K* wall collapsed till seals with edge of foot-flange. The top lead-through is sealed in at the same time;
d fire-cutting skirt *R* from the envelope;
e completed tube and exhaust stem

as used for degassing, for about 15 minutes at 300–400°; the annular seam between the optical flats in contact is then heated by radiation from a graphite ring which is itself heated by H.F. The seam is raised to sealing temperature as mentioned (below M_g) and held there for 30 seconds. This process (see BLEUZE, [3]DANZIN) has the advantage that the inner parts are protected from any oxidation or other damage by flame gases, it is hardly possible for mechanical stresses to build up, and the sealing process is combined with degassing. However, it is more expensive and therefore has not so far been introduced into mass-production.

See 10.6.I for use of low-melting glass solder for joining envelope and press.

Constructions of bulb-sealing machines. One can again distinguish two fundamentally different groups: those in which the work turns and the flames remain fixed in position, and the reverse. While the latter principle is almost only used on one-off production of the larger and more complex tubes, where rotation of the work would introduce the hazard of displacing previously adjusted components, the standard bulb-sealing machines for radio tubes and filament lamps operate with the work rotating on multi-position turntables like those of stem-pressing machines; the cycle corresponds to that of Figs. B 10-138 and B 10-139, where several operations are automatically carried out one after the other.

Figure B 10-140 shows an example of a 24-position, fully-automatic sealing machine for ordinary filament lamps (15–100 W) with vertical pinch and flare section; its output is 1250 per hour. As already mentioned in the discussion of the universal machine (Fig. B 10-127), the same machine can often be used to make the pinch and to join it to the bulb if it has rotating holders. The place for stem-pressing jaws is then fitted with holders for envelope and foot (Fig. B 10-127, IV). The process carried out by these semi- or fully-automatic machines is a series of operations; in the first table position, the foot is installed and the bulb dropped over; simple mandrels hold the feet, and the
[10.3] envelopes are clamped as in Fig. B 10-127. If a lead-through has to be sealed in the top

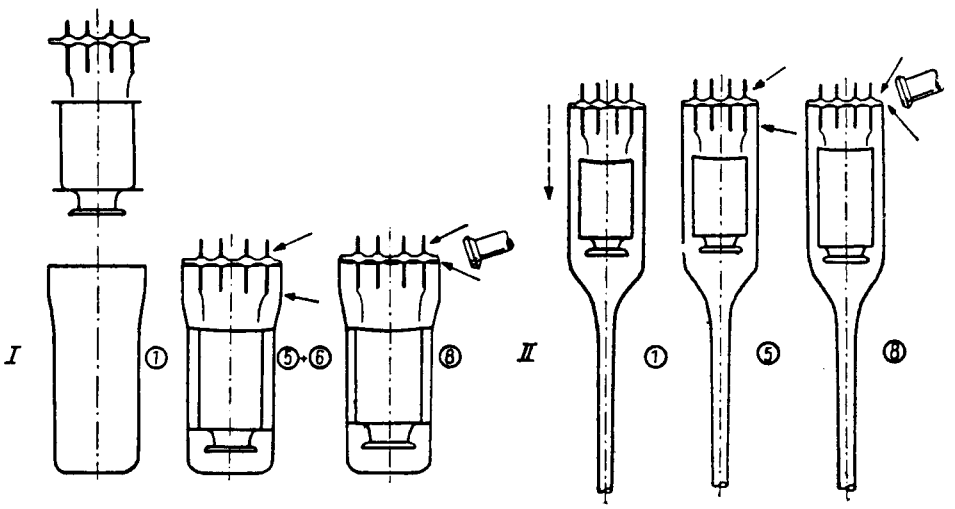
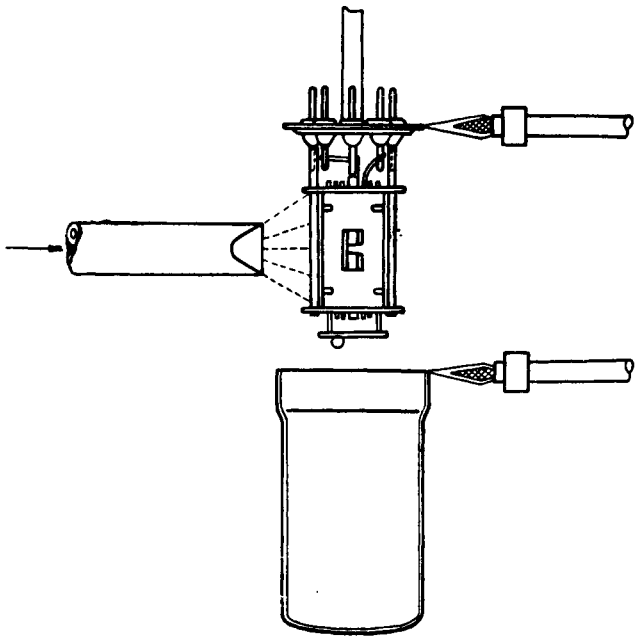


Fig. B 10-139 Schedule for sealing horizontal press-foot to tube envelope in 12 automatic steps

POSITION	I (ALL-GLASS TUBES)	II (MINIATURE TUBES)
1	Introduction of base and electrodes into envelope below	
2	Soft flame lowered on contact pins	60 °C
3	Sharp flame on contact pins	100 °C
4	Hotter (sharper) flame on pins	150 °C
5	Flame applied to envelope flame on pins	200 °C
6	As 5, flame on pins to heat to	300 °C
7	As 5, flame on pins to heat to	510 °C
	Sealing zone heated further	—
8	Sealing zone heated white-hot	Sealing zone heated white-hot by first application of flame at this point
9–11	Gradual drop in flame temperature to produce slow cooling	
12	Soft flame to pre-anneal	



[10.3]

Fig. B 10-139A Procedure for sealing foot to envelope of a radio tube with self-supporting electrode system, which, with its press-foot, is kept apart from the envelope while the glass is being softened, and is air-cooled until just before final sealing of base to envelope, when it is introduced into the latter ([2]KRATOCHVÍL)

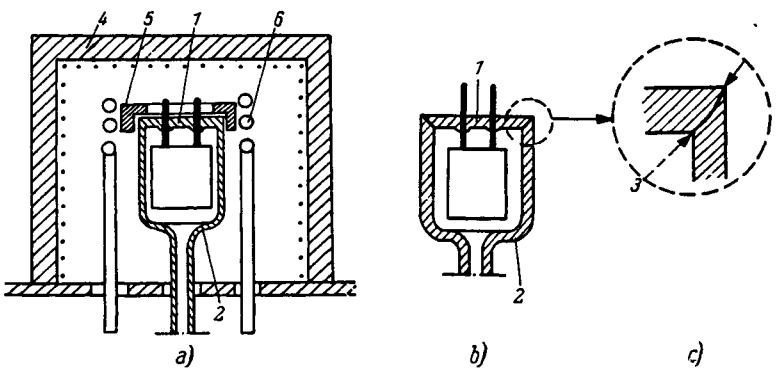


Fig. B 10-139B Vacuum-tight non-demountable joint between glass foot and envelope, made below the deformation temperature; both components have optically flat contact surfaces which are mated under pressure (BLEUZE)

1 foot with electrode system; *2* envelope with pump stem; *3* optically polished contact surfaces; *4* electrically heated external furnace (200–400°); *5* graphite ring for additional heating of contact zone to less than M_g (deformation temp. *ca.* 450–550° depending on type of glass); *6* H.F. work-coil to heat graphite ring. (a) complete unit; (b) and (c) illustrations of tube and seal zone

of the envelope for a radio tube (position *0*, Fig. B 10-138, *a*), a hole is blown in the top before insertion in the machine. The envelope is dropped over the foot so that the lead-wire projects through the hole at the top. A glass sleeve is passed over the lead-wire from above to provide filler for sealing. This seal is made at the same time as the wires are sealed in the foot (Fig. B 10-138). The turntable is stepped on either by foot-lever

[10.3]

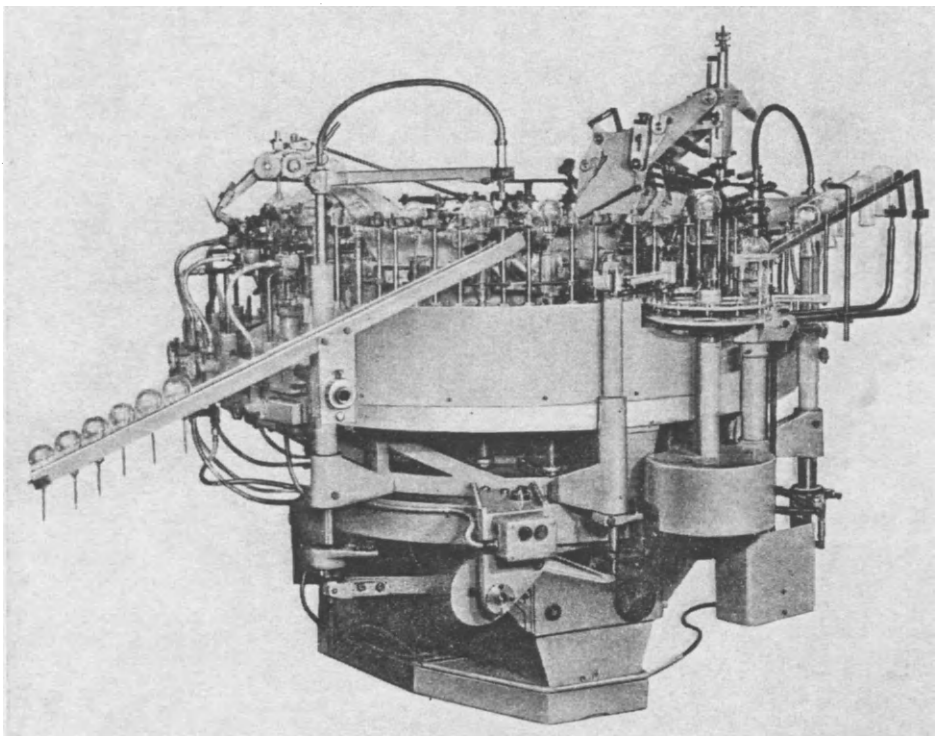


Fig. B 10-140 Fully-automatic stem-pressing machine with 24 positions, for making vertical pinches for 15–100 W lamps

Output: 1250/hr, type H 600 (made by G. BRÜCKNER, MASCHINEN-FABRIK, Coburg-Neuses)

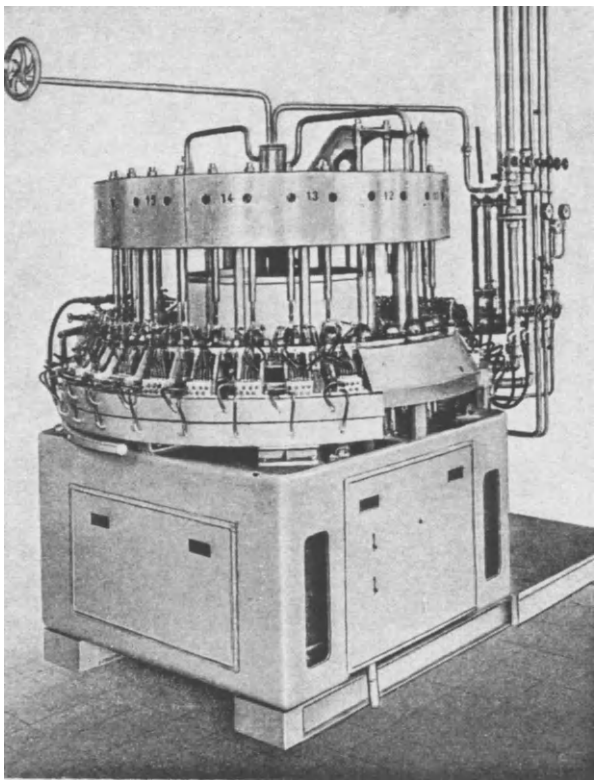
or automatically at certain intervals, so that the work is fed into fixed-position flames and goes through the stages corresponding to Fig. B 10-138. The last operating position serves as stated to re-heat the seal zone and shape it by a sliding former, or mold. The last position is often provided with press jaws which, as already mentioned, impress recesses in the base-socket area of the work as it pauses for a moment in the cycle.

Turntable machines are also used for sealing flat pressed bases to envelopes in radio tube manufature. Figure B 10-141 shows an example of a semi-automatic machine for miniature tubes of 15–23 mm dia.

The drive from the motor to the turntable and the rotary heads may be spur-gears, worm-gears, chain or belt transmission (see Fig. B 10-129).

For larger tubes and small numbers, it is general to use a semi-automatic vertical machine on a one-off basis (Figs. B 10-142, B 10-143). The first figure shows a rotary burner, fixed work set-up, and the second shows the reverse.

In the case of large tubes, such as TV tubes with 60 cm (24 in.) screens, multiple-position automatic turntable machines have already been built, as shown in Fig.



[10.3]

Fig. B 10-141 Semi-automatic 15-position machine for sealing flat press-foot to protective gas-filled envelope for miniature radio tubes (made by ELSTROJ-Prague, type ZM, output (max.) 600/hr; power input *ca.* 1.5 kW, *ca.* 1.8 m overall height)

B 10-143A and B. In the same way, long tubes with internal luminescent layers for low-pressure lamps are sealed at both ends to electrode-carrying feet on a serial system in special machines (see, e.g., Fig. B 10-125). Figure B 10-143C shows an automatic machine of this type with associated rotary annealing ovens.

It may be desirable that the flame heat, particularly intense with hard glass, be kept from reaching the whole envelope in the sealing process; this is specially the case with envelopes which have a side-tube, e.g. Hg rectifiers, and also with transmitter tubes having external Cu anodes. The neighborhood of sealing zone must then be wrapped with asbestos or protected by an asbestos or sheet-iron screen from excessive heat. A better way is to use sealing machines with horizontal spindles, called glass lathes (Figs. B 10-144,

B 10-144A). This device, originally developed by MARCONI, can be used for either vertical or horizontal work by tilting the whole upper section. It is important in these machines that the two parts to be sealed (e.g. envelope and electrode foot), which are mounted on two separate spindles, rotate as nearly in synchronism as possible. Figure B 10-145 shows the working cycle of a horizontal lathe of this type for sealing a dish foot *G* (Fig. B 10-137) with the glass tube *A* to which the Cu anode *C* has been previously joined by means of a metal sealing ring *B*. These lathes are also preferred equipment for sealing the metal rings to glass; see Chapter 30 for details.

[10.3]

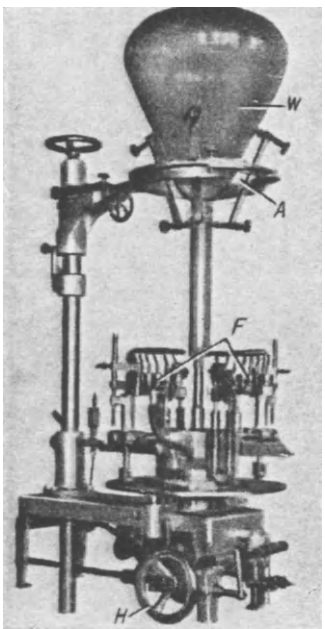


Fig. B 10-142 Vertical one-off sealing machine with rotary "fires" for large tube envelopes (made by SCHMIDT UND KLEINBERG GmbH)

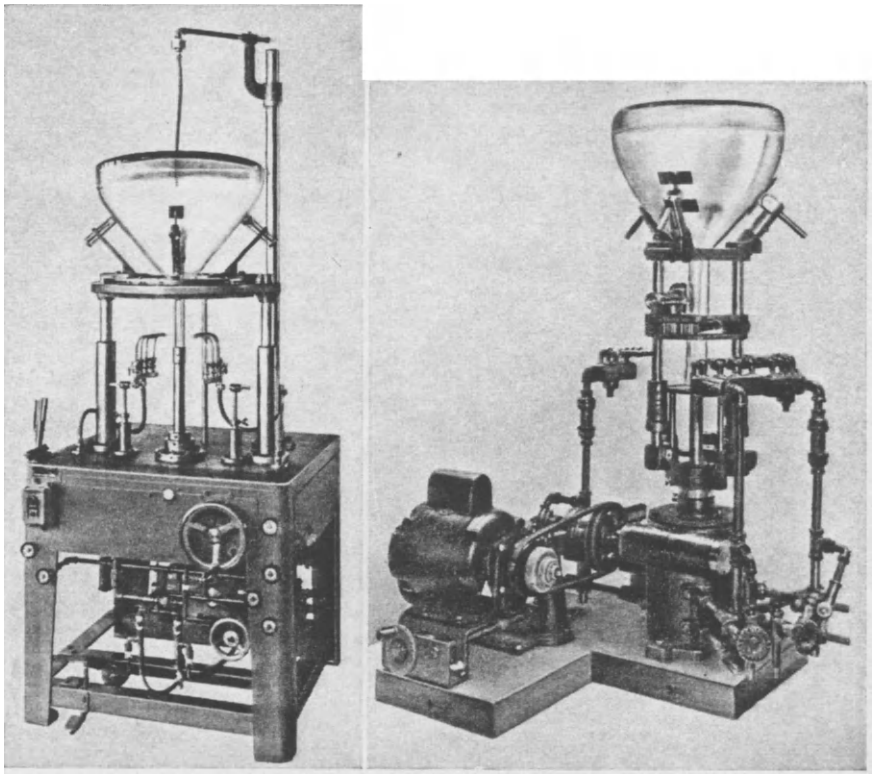
A head for the work *W*; *F* burners that revolve round the work; *H* hand-wheel for height adjustment of burners during cycle

With all such one-off sealing machines, as can be seen from Figs. B 10-142 to B 10-144A, the controls comprise not only a hand-wheel for setting the gap between the two rotating chucks but wheels for positioning the burners, quick-action levers for gas and air inlets, a control for setting speed of rotation (centrifugal action), a foot-brake to slow or stop the rotating work-piece and usually a press-button-operated valve for compressed air inlet to the envelope. The glass-blower generally prefers to supply the compressed air for blowing the seal by mouth, through a $CaCl_2$ drying tube and a rubber connecting line; this gives a more sensitive "feel" when pressurizing or (by suction on the line) reducing pressure and so partially collapsing the seal area.

Small flashlight bulbs are made by machines which make a vacuum-tight seal between the lead-wires and filament (already mounted) and glass foot, and at the same time join the foot to the bulb in one operation. A pumping stem, protected before joining to the lamp by an inner Cu sleeve, is sealed in during the same operation. Figure B 5.4-13 makes the details clear.

On mass-production, the automatic pumping system (which see in 10.5) is joined directly to the bulb-sealing machine, as too long a pause in operations due to conveying the work from one to the other is generally undesirable, particularly when air-sensitive components in the envelope such as oxide cathodes might be damaged. This has been taken a step further by the construction of combined sealing and pumping machines

[10.3]



I II

Fig. B 10-143 Vertical one-off sealing machine for large tube envelopes

I work rotated by gear-wheel; burners fixed position; above: protective gas supply line. Output 6–12 sealing operations/hr. Height 1.5 m. (Type KESM I, made by SCHMIDT UND KLEINBERG, Neu-Ulm/Donau)

II work in holder rotates with stand; 3 stationary "cross-fires" (Type 102-VI D, made by EISLER ENG. Co., Newark, N.J., USA)

("seal-exhaust"). This means that the furnace lever otherwise needed on automatic pumping machinery for heating the envelope can be wholly or at least partly removed, since this process will have already taken place while sealing the lead-wires (KOSACK). These seal-exhaust machines are used mainly in filament lamp manufacture. Figure B 10-145A shows a so-called "Anschlussgruppe" (combined operation unit) which, besides evacuating the lamp, gas-fills it, seals it off, applies the lamp base, marks it, tests it and then packs it; the unit usually requires only one person to operate. To give some conception of the capabilities of these fully-automatic machines it should be

pointed out that a 16-position unit can produce up to 2000 per hour (ZIMBER). Construction of a machine of such high output obviously requires special measures. For instance, the jaws which hold the work have to be cooled so that installation of stem or envelope does not cause them to crack from contact with machine parts just previously heated by the working flames.

[10.3]

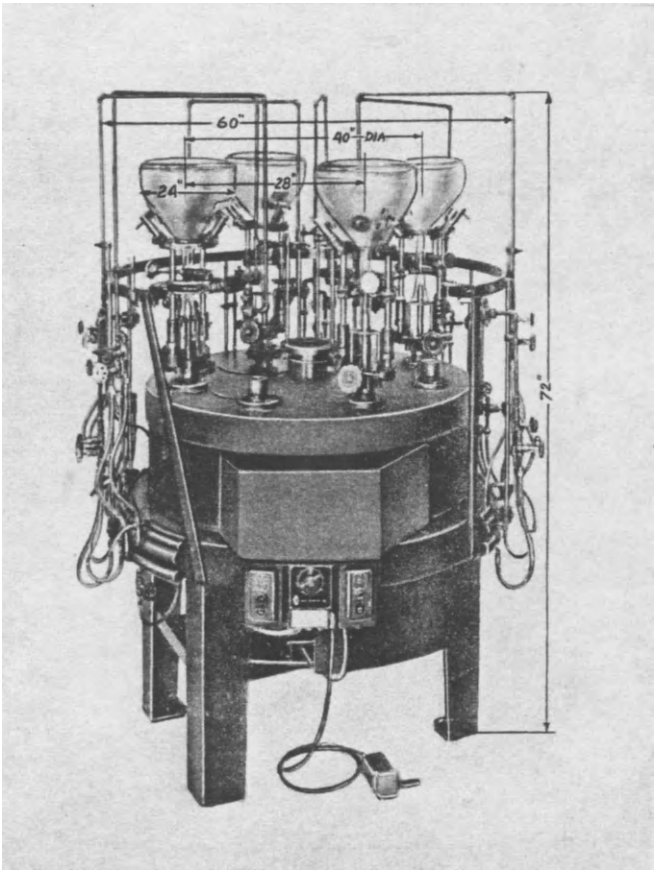
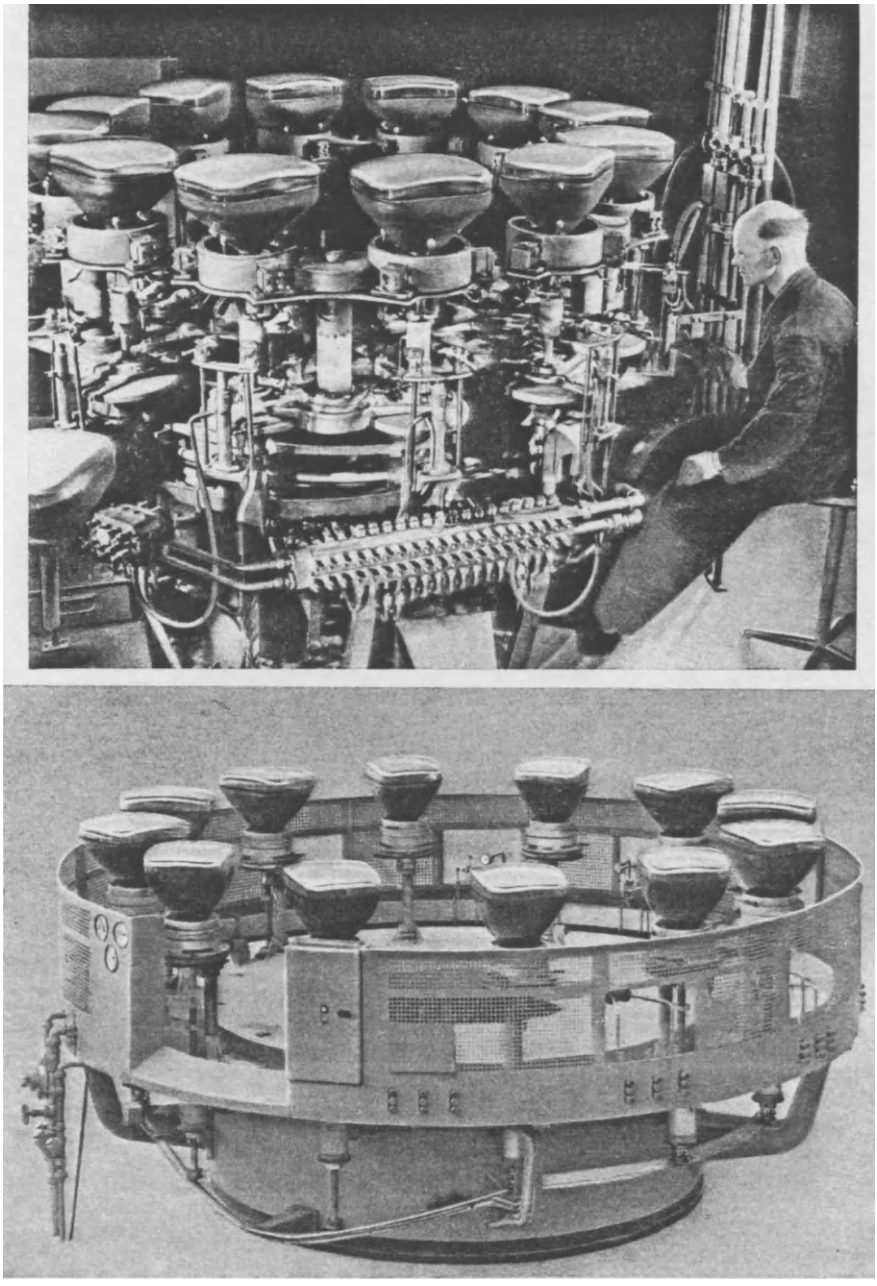


Fig. B 10-143A Semi-automatic bulb-sealing machine (up to 24 in. dia.) for TV tubes; seals envelope to the foot on which the electron gun is mounted (type 57–8–4 CTL, made by EISLER ENG. CO., Newark, N. J., USA). Dimensions are marked in inches

Recently, 24-position seal-exhaust machines have been built for radio tubes (Fig. B 10-145B, and 10.5).

4. *Special machines for glass-working.* Besides the machines treated so far, which take up most of the machine-shop of a tube or lamp works, there are often a number of other special pieces of equipment, varying with the type of product.

(a) One of these is the so-called hub/anchor machine required in lamp production.



[10.3]

II

Fig. B 10-143B Special automatic turntable machine for sealing envelope collar to glass cone of TV receiver tubes

I photograph taken at PHILIPS ([11]ANON.)
II photograph taken at TELEFUNKEN Röhrenfabrik Ulm (from HÜHN)

They provide a glass button or lens-headed stem with the Mo hooks (anchors) that carry the W filament of ordinary lamps (Figs. B 3.2-23, B 3.3-8). Figure B 10-146 sketches out the mode of operation. A length of glass rod (at *A*), which may be previously sealed to the lamp-foot, is set in a holder with limit stop. At the next positions *B* and *C*, reached by step-switching the turntable, the upper end of the rod is heated and then

[10.3]

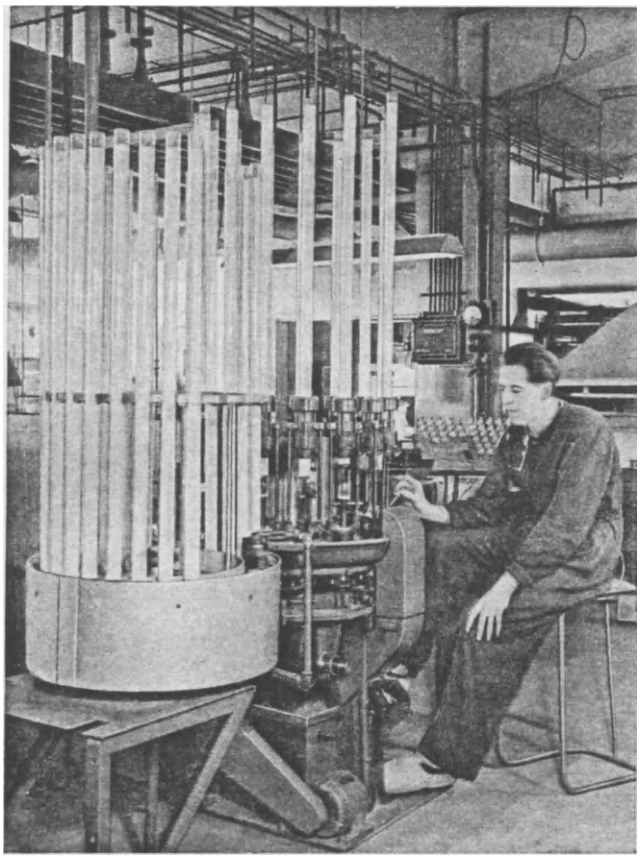
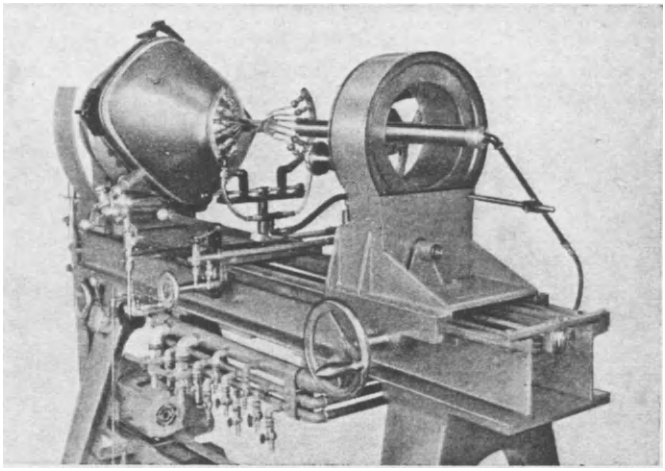


Fig. B 10-143c Sealing pinch plus electrodes into luminescent tube lamps on a special semi-automatic machine (photograph taken at PHILIPS (from [10]ANON.))

Left foreground: rotating annealing oven for the tube ends after sealing. The tube is reversed and a foot sealed into the opposite end

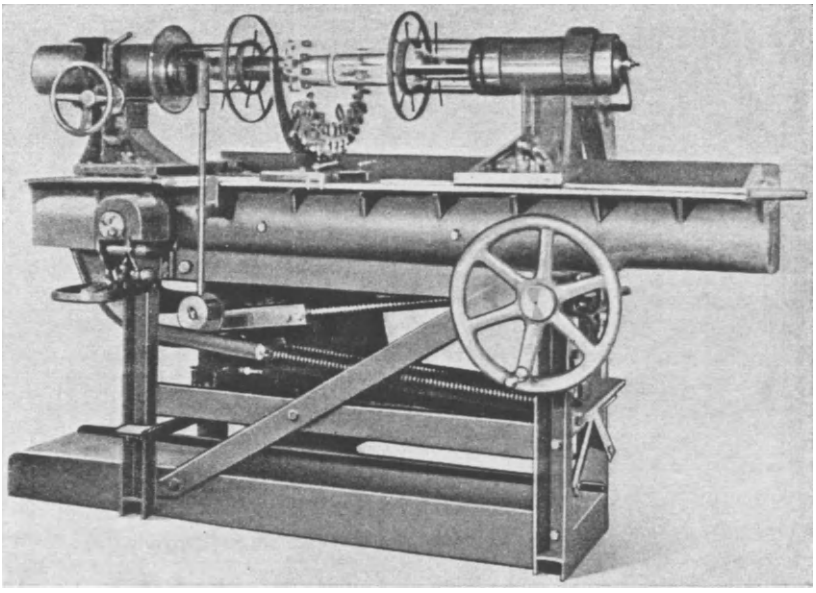
upset to form the lenticular head. Finally, at *D*, wire automatically fed from a spool is embedded in the still-soft head, cut to length, and at the same time the hooks are formed. The work is then revolved at *D* through an angle, wire from the spool is embedded and cut off again until a complete turn has been made and the table stepped on to position *A* where the finished work is removed and replaced by an unfinished part. The device is motor-driven. A hand-wheel is provided for slow operation. The upset ram for making the head, the wire-feed mechanism and the hook-former and cut-off



[10.3]

Fig. B 10-144 Large glass lathe (type HESM 1). Made by SCHMIDT UND KLEINBERG, Neu-Ulm/Donau

Reversible and continuously variable between 1 and 5, and 10 and 50 r.p.m.; two synchronous heads driven by rim gears, with interchangeable holders or iris-type chucks, the right-hand one and the burner nozzles both adjustable in position on the lathe-bed by means of hand-wheels



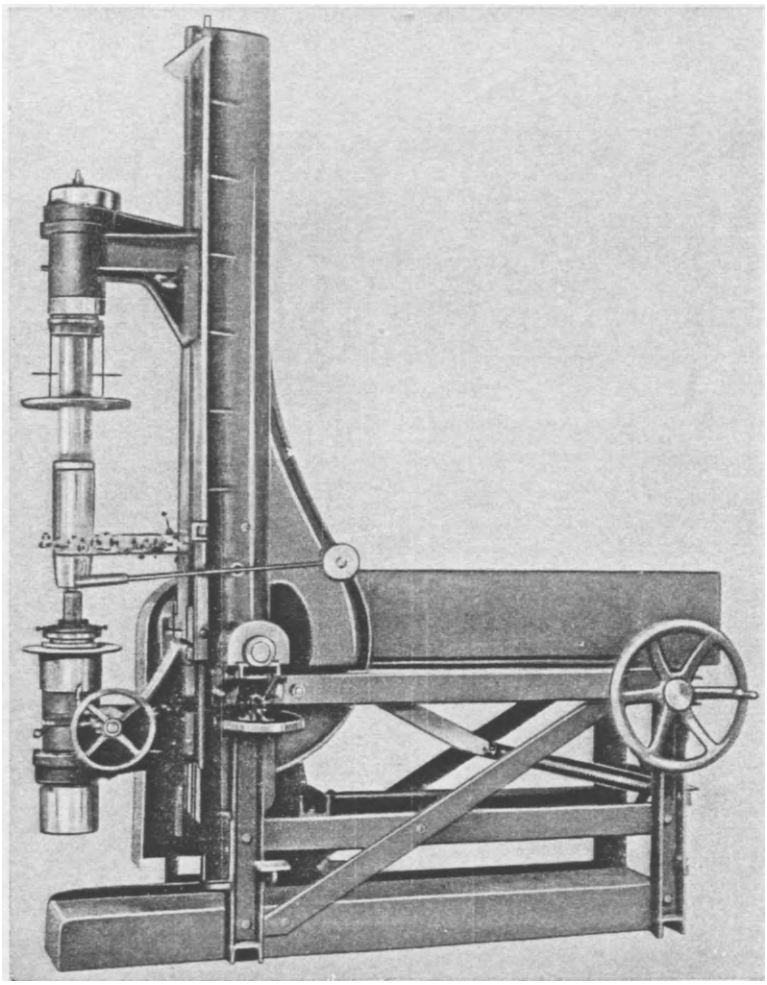
I

Fig. B 10-144A1 Large MARCONI glass lathe with tilting bed (DAVIES)

I 2.6 m long with spindle axis horizontal, 1.3 m height at axis, max. length of work-piece 1.2 m, max. work diameter 40 cm

tool are all cam-operated. A Maltese cross is used to move the table from position to position. On mass-production, the automatic machines are designed to embed the hooks all at one time, not seriatim. The small machine shown in Fig. B 10-147 produces about 350 parts per hour with 5 anchors.

[10.3]



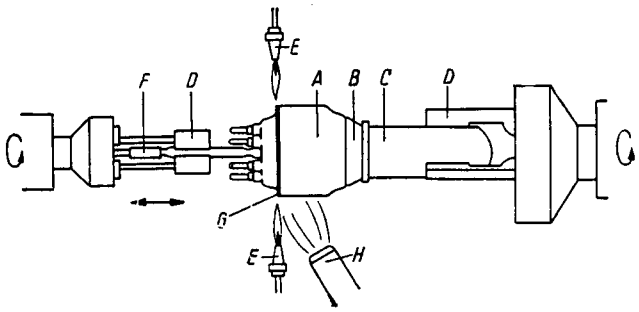
II

Fig. B 10-144A_{II} As A_I, spindle axis vertical

Other special glass-working machines have recently been installed to make miniature and sub-miniature tubes. Without too much reconstruction, the automatic machinery that has been in use for a long time for making medical ampoules can often be used. Only the most important types are considered here.

(b) *Machines for making cylindrical envelopes of miniature tubes, 15–22 mm dia.* Manufacture follows the scheme of Fig. B 10-148 in a so-called "automatic end-sealing

machine" (Fig. B 10-148A). Glass tubes are cut to about double the length of an envelope and are laid horizontally on four revolving rollers, heated in the centre by a flame and moved serially by a cam-like drive from one working position to another as in Fig. B 10-148; in each working position, upper and lower flames directed to the heating zone pre-heat, collapse, fire-cut and round off both the ends of the resulting envelopes.



[10.3]

Fig. B 10-145 Sealing dished glass base (*G*) to glass envelope (*A*) of a transmitter tube on horizontal glass lathe ([8]ESPE)

E circle of burners, mounted on sliding carriage on lathe-bed; *H* general preheating flame; *B* metal ring sealed to *A* and hard-soldered to Cu anode *C*; *D* chucks for work-pieces; *F* compressed air inlet for blowing the seal

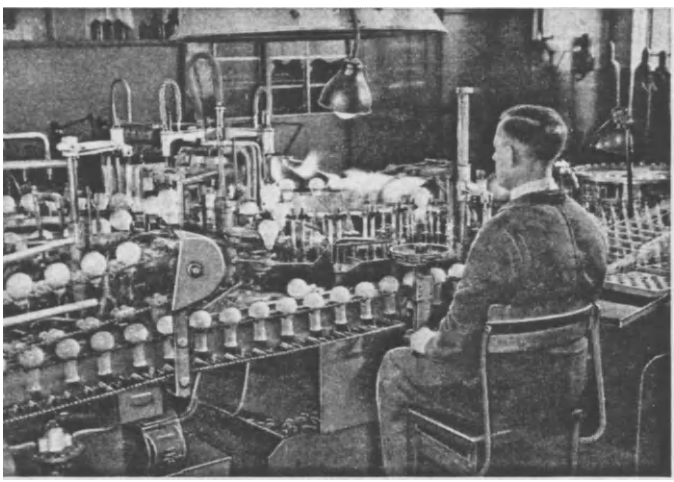


Fig. B 10-145A So-called "combination group" for making filament lamps; it seals in the leads, exhausts, gas-fills, seals off, applies socket-base, stamps, tests and packs standard lamps ([12]ANON.) (photograph taken at PHILIPS)

(c) *Small bulb-blowing machines.* Glass tube from the works is cut to length and laid in the magazine of a machine similar to that in Fig. B 10-149 and is then automatically blown to shape. In another type (Fig. B 10-150), the bulbs are blown continuously from a 1.2 m length of glass tubing; after heating up and sealing, the end of the tube is placed in hinged jaws of suitable shape and blown by compressed air. The jaws are obviously

[10.3]

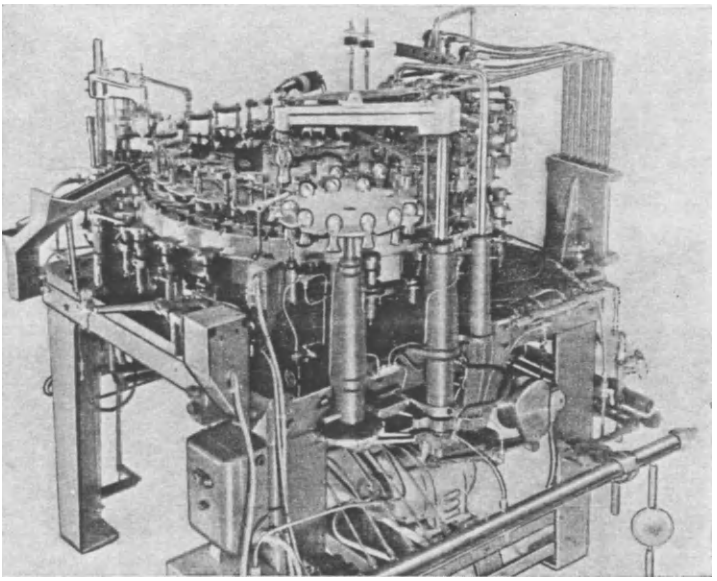


Fig. B 10-145B Automatic seal-exhaust machine, 24 position, for radio tubes (made by EISLER ENG. Co. type No. 57-MX-D)

Output 1000–1800/hr

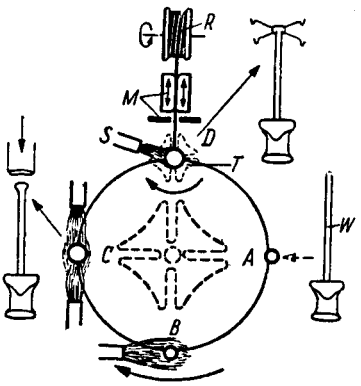


Fig. B 10-146 Simplified design of 4-stage hub and anchor machine

A installation of work-piece *W* on revolving ring; *B* heating upper end of glass support hub; *C* upsetting the hub to form head after further heating of glass; *D* embedding wire anchors or hooks in hub; *S* pencil flame to heat embedding points; *R* wire spool; *M* wire feed device, cutter, and hook-forming tool; *T* Maltese cross at *D* for rotating the work-piece stepwise

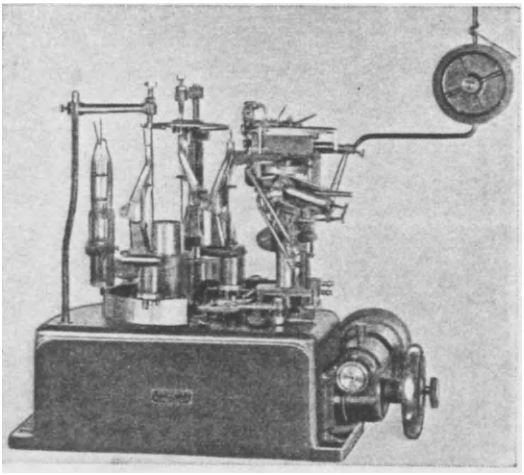
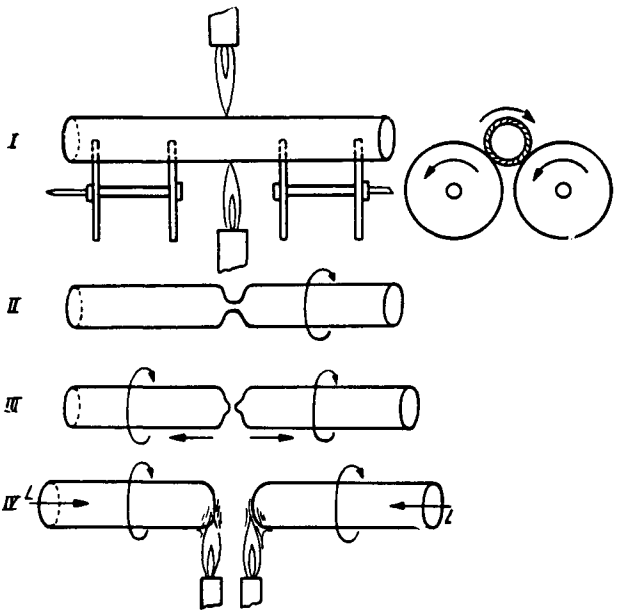


Fig. B 10-147 Machine corresponding to Fig. B 10-146 (made by GLADITZ GmbH)



[10.3]

Fig. B 10-148 Manufacture of cylindrical envelopes for subminiature tubes

I glass cut to length, laid horizontally on 4 rotary disks, flame-heated centrally (right: side view)
II collapse of heated zone
III fire-cutting, two half-sections heated and separated
IV compressed air blown in from *L* and rounding off

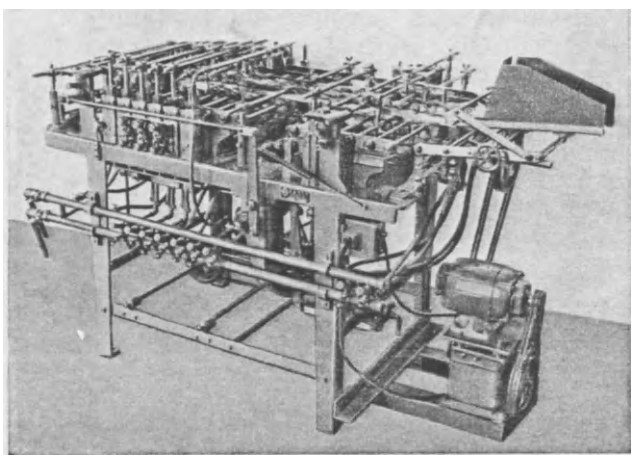


Fig. B 10-148A Automatic machine for making cylindrical envelopes for miniature tubes as shown in Fig. B 10-148 (made by AMBEG, Berlin-Schöneberg, type B 4g)

Glass dia. 8–26 mm, smallest individual length with flat top 40 mm, witb dome 50 mm; largest length 200 mm. Output depends on diameter, 1200–2400/hr

interchangeable to match the desired bulb. O_2-burners cut the bulb from the tube, whose end is resealed, and the cycle begins again.

(d) *Exhaust-stem sealing machines.* Since the press with electrodes of miniature tubes is too small to take a stem, as can be seen in Fig. B 10-131, II, III, this machine attaches one to the dome or top of the envelope. Figure B 10-151 shows an example of such
[10.3] a machine, which blows an opening in the envelope top and automatically fuses the stem to it.

(e) *Machines for making miniature envelopes with exhaust stem.* Envelopes for subminiature tubes (<10 mm dia., *ca.* 30 mm long) can be made individually from the

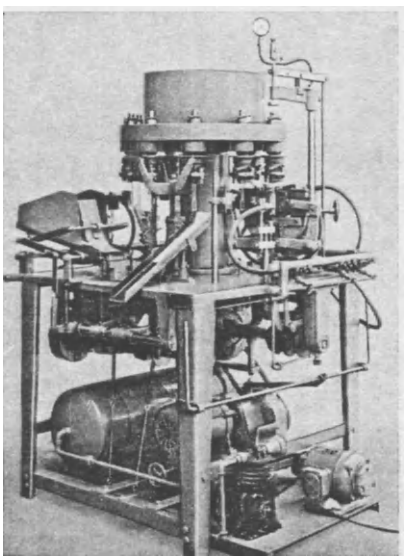


Fig. B 10-149 Bulb-blowing machine for automatic manufacture of spherical or other small envelopes from pre-cut glass tubes 8.5–23 mm dia. (type BL, made by AMBEG, Berlin-Schöneberg)

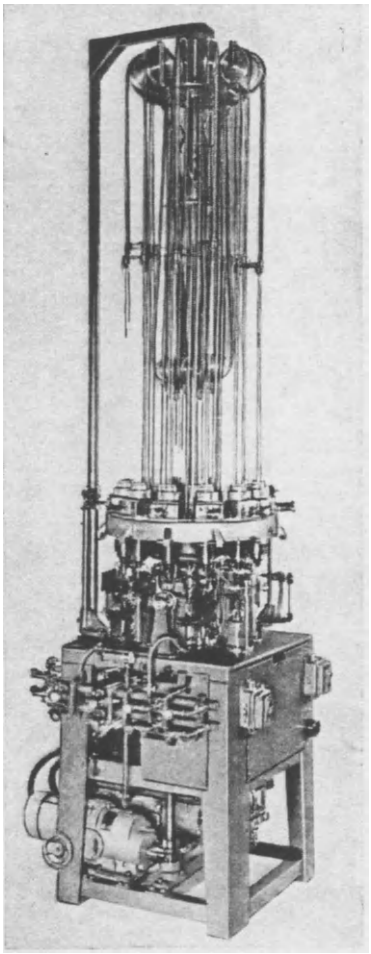


Fig. B 10-150 Automatic bulb-blowing machine with 12 positions for blowing envelopes from glass tube sections 6–21 mm dia. (type KOBLA 12, made by SCHMIDT UND KLEINBERG, Neu-Ulm/Donau)

Diameter of any radially-symmetric envelope up to 40 mm; output 800–1200/hr according to size

vertical glass tube so as to incorporate the stem at the same time. Figure B 10-152 shows the process; a glass tube *A* is clamped between two rotary chucks and is heated at the cut-off zone (I); it is then slightly collapsed at two points by shaping wheels *E* and at the same moment the intermediate section (*B*) is inflated (II). These steps form

the basis for the formation at stage III, where the two sections (*C*) and (*D*) are drawn apart, of a cylindrical length (*F*) whose diameter is constant everywhere. Without step II this section would contract too much in the center, forming two cones. A cutter (see 10.3.VII) separates this thin tube in the center *G* and the upper section of tube *C* is cut at *H*; two similar envelopes *V* with their stems are thus made in one operation.

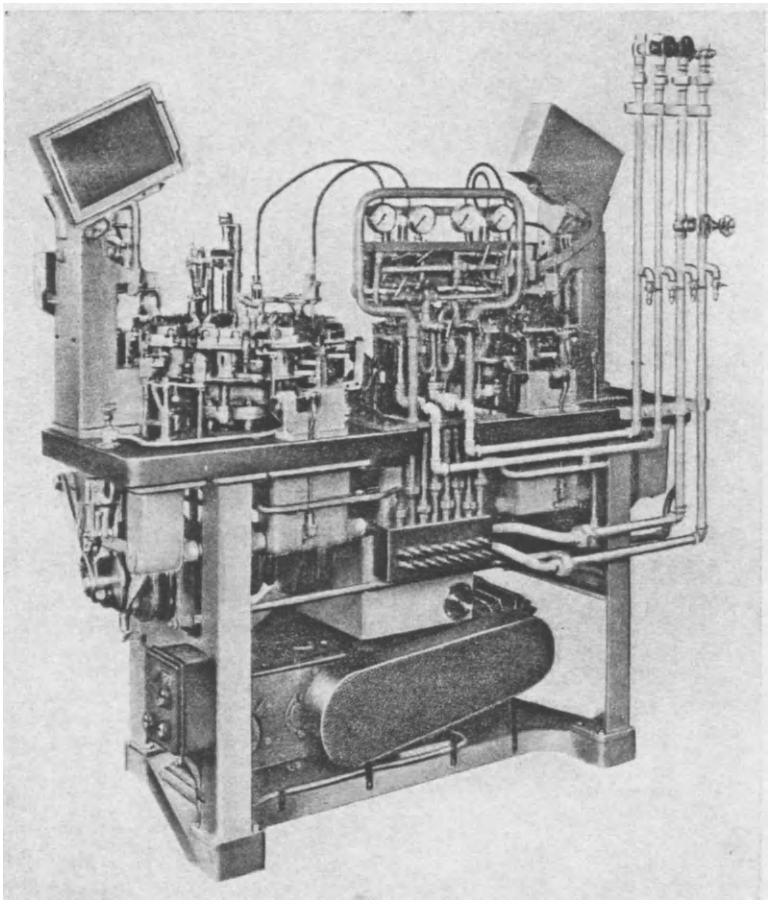


Fig. B 10-151 Automatic pumping-stem sealing machine for miniature radio tubes; stems 3.2 mm on domes of 15–23 mm dia. envelopes (made by ELSTROJ-Prague, type 11A)

The machine has two separate turntables each with 9 positions, and employs O_2—H_2 flames. Output 360/hr. power input *ca.* 1 kW; height 1.5 m; length 1.5 m; width 0.65 m

(f) *Sub-miniature tube-pinching machines.* No flat base is sealed into *sub*-miniature tubes but the open end of a round or oval tube is pinched at the plane of the lead-wires after the electrode system, held between two mica plates, has been introduced (Fig. B 10-153). This technique has been known for a long time in connexion with very small lamps such as those for telephone indicators and medical diagnostic lamps; it has

recently attained importance in making miniature tubes for amplifiers in portable equipment such as deaf-aids. The process produces a vertical pinch which, in contrast to the well-known classical pinch (as shown in Fig. B 10-131, I), is not placed inside the envelope but projects from it. The leads in the pinch are usually sealed vacuum-tight to glass beads beforehand, a process carried out automatically (Fig. B 10-152, IV).

Space-saving in small portable equipment has led to manufacture of oval-section sub-miniature tubes, a process illustrated in Fig. B 10-154. In order to increase the leakage path across the pinch between leads, profiled pinches have been made as [10.3] shown by some examples in Fig. B 10-155 (²EISLER).

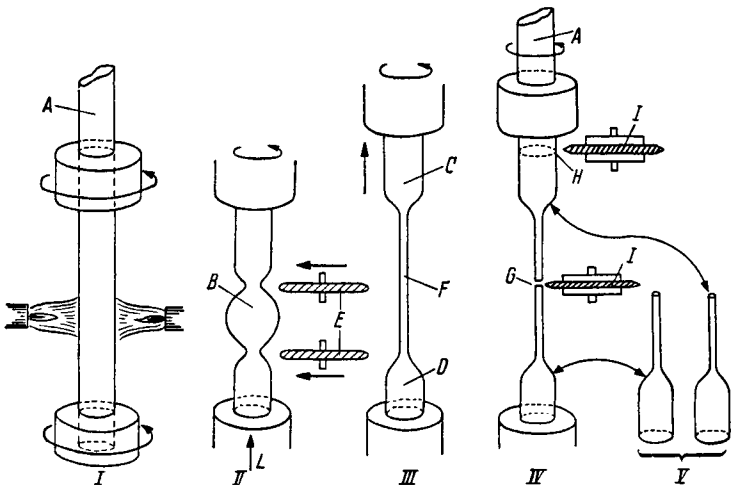


Fig. B 10-152 Process for making of glass envelopes and pumping stems simultaneously for sub-miniature tubes. Electron tube diameter below 10 mm

I glass rod *A*, upper length "endless", clamped vertically in two synchronous chucks, heated in center by stationary flame burner

II depressions formed by shaping wheels *E*, of central section *B* blown out with compressed air *L*

III separation of glass tubes *C* and *D* by raising upper chuck and formation of exhaust stem *F*

IV cutting of stem at *G*, and of upper tube *C* from the feed tube at *H*, both by water-cooled spray-disk *I*, the two cutting zones having been heated before, release of lower tube *D* from bottom chuck, upper tube *A* fed into working position *I*

V the envelope and stem, produced in one operation

(g) *Machines for sealing the panels of TV tubes to the metal cones.* A frequent operation resulting from introduction of television is sealing the picture panel to the cone of TV tubes, or sealing glass panels into video tubes; where glass-cone tubes are involved, this job is generally one for the glassworks where the two components are hand-made in one piece (Fig. B 10-108, X); more recent manufacture employs electric resistance welding (see 10.3.V). Metal cone tubes can be made by H.F. heating the rim of the cone to seal it to a circular panel (see Chapter 30); if the panel is rectangular, it is simpler to use a vertical sealing machine of the type in Fig. B 10-143; Fig. B 10-156 shows a special American construction. See EDENS for details of sealing machines for joining TV-tube square panels to the cone with glass-blowing burners.

10.3.III. *Thermoplastic Glass-working by Radiant Heating (without Contact Between Glass and Open Flame)*

Although this method is used much less than flame-working, i.e. thermal convection, it is effective in certain special cases of vacuum technology.

The method has been successful primarily in the manufacture of so-called "plug seals". The glassworks supplies a clear glass stopper or plug with holes parallel to the

[10.3]

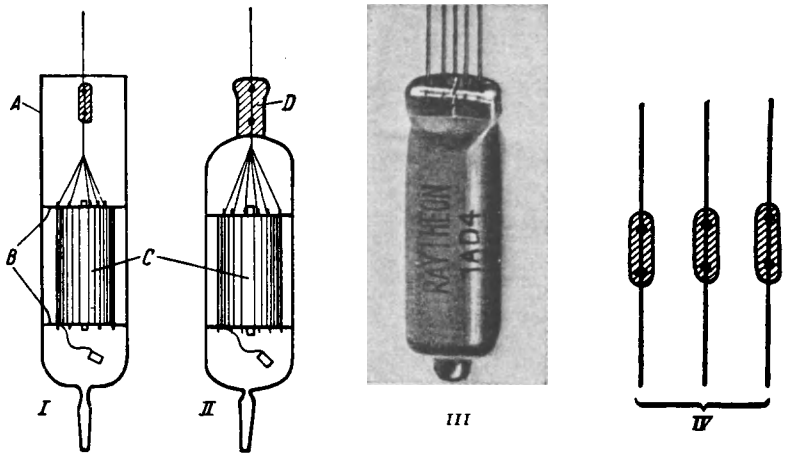


Fig. B 10-153 Manufacture of sub-miniature tubes

I the electrode system *C*, mounted on 2 mica plates *B*, is introduced into envelope *A*; II *A* is heated and then pinched as in Fig. B 10-128A or B; III view of pumped tube with its flat pinch; a D.H. pentode 1 AD 4, cathode supply 1.25 V, 100 mA, plate power 45 V at 3 mA, made by RAYTHEON; IV glass-beaded leads before electrode assembly is mounted

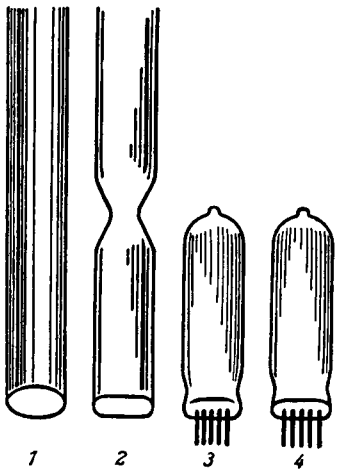


Fig. B 10-154 Manufacture of flattened (oval) sub-miniature tubes ([2]EISLER)

1 cylindrical initial tube; *2* after flattening out lower part and necking at the seal-off area; *3* pre-pinched leads; *4* after forming seal area

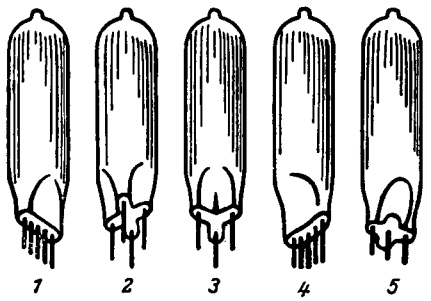


Fig. B 10-155 Cylindrical miniature tubes with various shapes of pinch ([2]EISLER)

1 flat pinch; *2* cross-pinch, *3* star pinch; *4* re-entrant pinch; *5* profile pinch

long axis, inside a metal tube which has usually been pre-enameled. Pre-glassed lead-rods or wires are inserted in the holes and the unit is laid on a graphite disk (as in Fig. B 10-267) to prevent leakage of glass. This arrangement is now placed in an electric furnace and heated to softening point of the glass so that vacuum-tight joints are made between the plug and the glazing of the metal tube and leads. (See ADAM for further details.)

See 10.6.III for making plug seals, and moldings of glass powder (chiefly H.F. electron-tube presses with lead-throughs), by sintering under radiant heat; see 10.6.I,
[10.3] for making vacuum-tight joints with "glass solders", where radiant heating is the usual method of preparation.

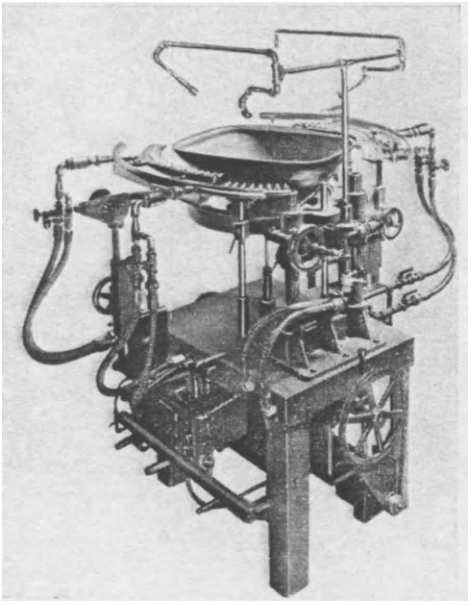


Fig. B 10-156 Vertical sealing machine for joining the rectangular panel of a TV tube with the metal cone (cf. Fig. B 6.5-3 a). Type No. 57-TEL-T, made by EISLER ENG. CO., Newark, N.J., USA

See LAUDER on the application of electrical radiant-heat sources combined with flames for sealing large-diameter tubes; see 10.3.VIII on annealing glass after working by thermal radiation in a tempering furnace or by gas-heated IR radiators made of ceramic materials.

Thermal radiation plays at least some part in the glass-working method described in the next section.

10.3.IV. *Thermoplastic Glass-working by Thermal Conduction*

There are cases in tube construction where the recommended method is to apply heat largely or wholly by thermal conduction from a metal, itself heated by H.F.; this is to melt the glass in contact with the hot metal, or other pieces of glass heated similarly. Figure B 10-157 shows an example where a metal knife-edge *2* in contact with the end of a glass tube *1* is heated by H.F. energy supplied to a concentrator *3* from work-coil *4*. (For more detail on concentrators, see 9.3, especially Figs. B 9.3-45, B 9.3-46.) The

temperature is raised to the point where the glass tube softens at the knife-edge contact line with tube *2*, slides down guide-tube *6* to stop-flange *7* by dead-weight, and makes a vacuum-tight joint with the knife-edge. If a quartz bell-jar is placed between H.F. coil *4* and concentrator *3*, the process can be carried out in a neutral protective atmosphere of, say, N_2. Obviously, this kind of seal, also using H.F., can be undertaken in a glass lathe (Fig. B 10-144), if the usual ring of burners is replaced by an H.F. coil concentric with the annular seal area and the metal tube is pressed into the glass tube-end, once it is sufficiently soft, by shifting the spindles towards each other. If a metal tube, whose O.D. is slightly less than the I.D. of the glass tube, is inserted in the latter [10.3] for a distance equal to the desired length of the seal area, and the glass is heated by

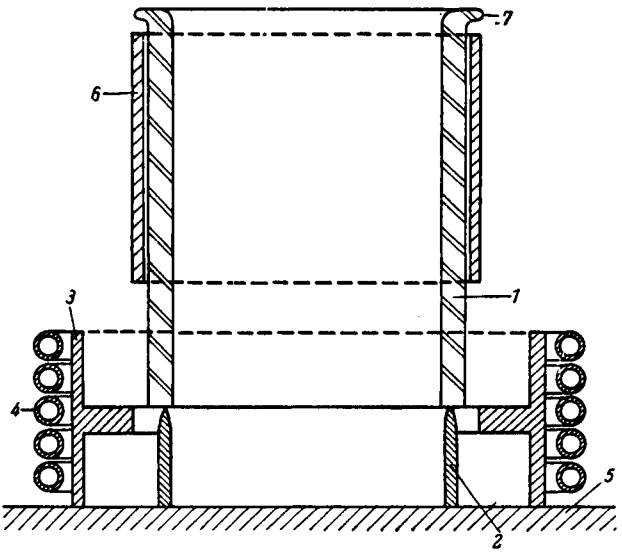


Fig. B 10-157 Example of thermoplastic forming of glass by thermal conduction

Sealing a glass tube *1* to the knife-edge of a metal tube *2*, heated with a concentrator *3* and H.F. work-coil *4*, to red-heat. *1* drops under its own weight in guide *6* over edge of *2*, to a distance set by stop-flange *7* (LUPÍNEK)

radiation and conduction with an H.F. source, the soft glass tube-end can be pressed against the metal by a spatula; in this way, the combination of glass-lathe and H.F. can produce an external glassing of the metal tube. If internal glassing is desired, the softened glass zone can be pressed against the inside of the hot metal tube by sudden increase in rotational velocity of the lathe (centrifugal force). Further examples of H.F. joining are given in the treatment of special sealing metals in Chapter 30, sections on Kovar and Housekeeper seals.

There are processes where the outer surface of the glass near the seal are metalized, and the metal coating is heated until the glass beneath is soft (Fig. B 10-158); they have not found their way into common use; neither have those where the flat glass press is sealed to the envelope by H.F.-heated graphite or metal rings, partly by thermal conduction and partly by radiation instead of flames (Fig. B 10-159). However, the

latter process has been used successfully to make vacuum-tight joints between envelope and press-foot of miniature tubes by application of a glass enamel that softens at a low temperature (see 10.6.I), and also in sealing two optically flat compressed contact areas as already described with reference to Fig. B 10-139B.

10.3.V. *Thermoplastic Glass-working by Resistance Welding*

This is still partly in the development stage, applying mainly to hard glasses; as with metals, Joule heat is produced by passage of current through the parts to be joined and melts or softens them and therefore can be used to join them. Since glass does not conduct enough current until raised to high temperature, auxiliary flames must be used to do this; the starting temperature for Pyrex is about 500–600°, and such appropriate temperatures must be reached at least in the weld zone for resistance heating, and the actual welding, to begin.

[10.3]

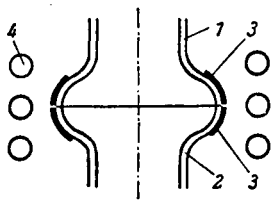


Fig. B 10-158 Sealing two glass tubes *1* and *2* by heating their ends by conduction from metal layers *3*, which have been applied to the surface of the seal and are heated by H.F. work-coil *4* (VIOLET)

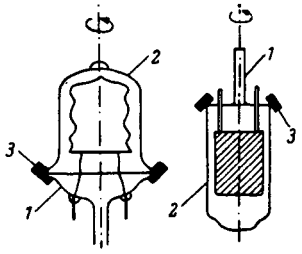


Fig. B 10-159 Sealing flat or dished bases *1* to tube envelopes *2* by electrically heated metal rings *3* which conduct heat to the sealing edges and are in direct thermal contact with the glass (VIOLET)

In one method ([1,2,3]GUYER, [1,2]SHAW), the weld zone, which may consist of two abutting Pyrex tubes, is superficially heated to about 600° with two pencil flames from oxygas burners arranged opposite to and electrically insulated from each other (Fig. B 10-160); or they may each be held by an operator, the operators being mutually insulated (Fig. B 10-160A). A 10 kV potential difference, at 10^5–10^7 c/s, is now applied across the burners. The free-burning flames now act more as a pair of flexible current leads than as sources of heat, and are also variable series resistors. Once the glass has been sufficiently pre-heated, H.F. current now raises a narrow path through the whole interposed volume to over 1000° by Joule heat. The nearby region is not softened and the glass surface is not subjected to flame heating or to excess evaporation. The weld temperature is more easily and reproducibly adjusted than when flames are used. Optically ground hard-glass windows can be sealed quickly to the ends of glass tubing without softening or deformation.

Where large diameters are involved, e.g. thick panels sealed to glass cones of TV tubes, a recommended method for homogeneous heating of the weld seam is to spin the work on a glass-lathe while welding; pre-heat cross-fire burners of the ordinary oxygas type should be set up between the two electrically conducting flames (Fig. B 10-161).

The weld voltage has to be higher in this case than with ordinary glass-tube joining, since the current path in the glass is longer. A "soft" voltage source at *standard* 50-cycle mains frequency should be used. A typical circuit diagram is given in Fig. B10-161. According to [2]SHAW, an appreciable fraction of the output of American commercial

[10.3]

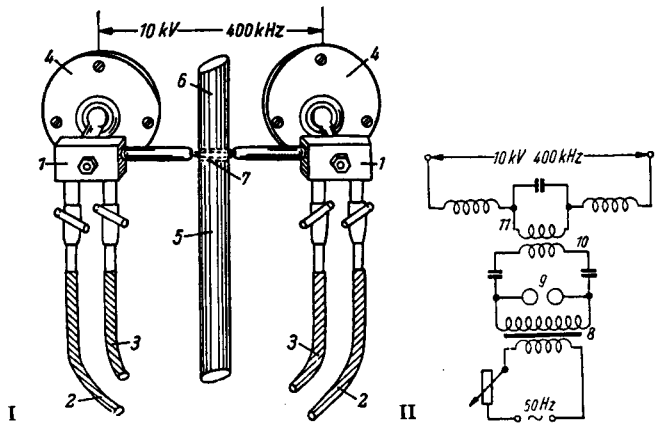


Fig. B 10-160 Resistance welding of glass (GUYER)
I set-up: *1* oxygas burner with mixing chamber and valves; *2* rubber tubing for O_2; *3* rubber tubing for gas; *4* insulated holders for burners; *5* and *6* glass tubes to be welded; *7* weld zone. II circuit diagram: *8* H.V. transformer; *9* spark gap; *10* H.F. transformer; *11* H.F. oscillator tank circuit

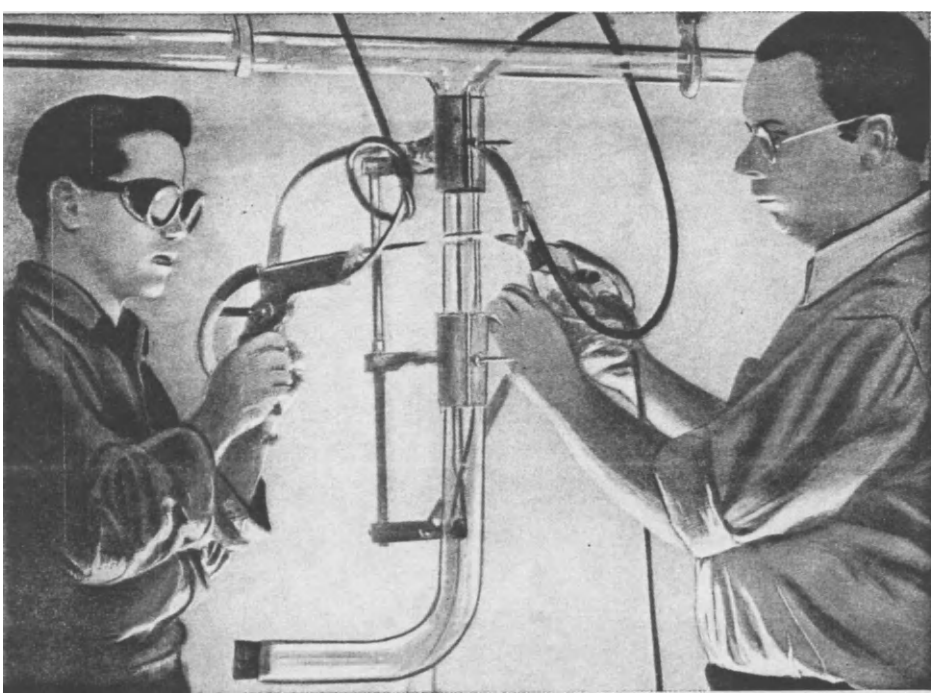


Fig. B 10-160A Resistance welding a glass pipe-line by process in Fig. B 10-160, using H.F. current supplied by two mutually insulated operators ([3]GUYER)

TV tube with glass cones is today electrically welded. See also EROSS for details of the apparatus.

WRIGHT gives details of another modern example of resistance welding, the new type of floodlight lamps where the filament and its leads, the metalized glass reflector and the front glass are all welded in a unit (Fig. B 10-161A).

[10.3]

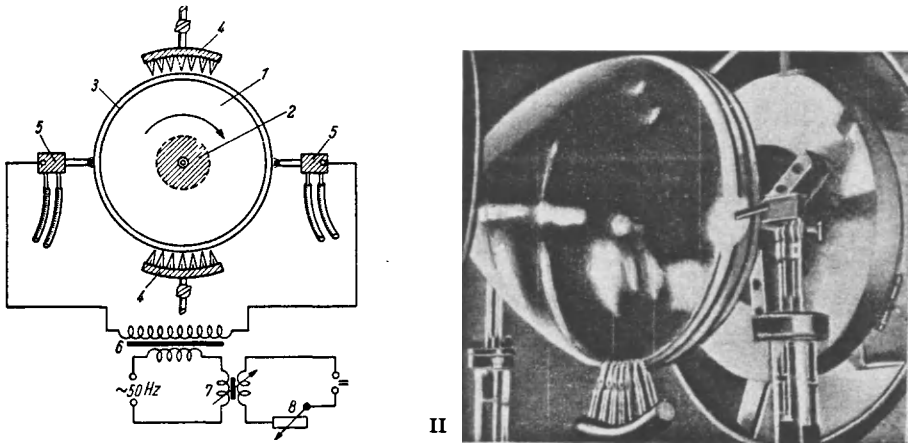


Fig. B 10-161 Sketch (I) and photograph (II) of arrangement for electrical welding of large glass panels to cones of TV tubes, or to the reflectors of floodlight lamps

1 front view of picture window panel rotating on a glass lathe, clamped by holder *2* so that its sealing edge is held against the edge of the glass cone; *4* ring burner for preheating weld zone *3*; *5* two oxygas burners set on a diameter and electrically insulated from each other; *6* H.V. transformer *ca.* 20 kV; *7* saturable reactor; *8* control resistance

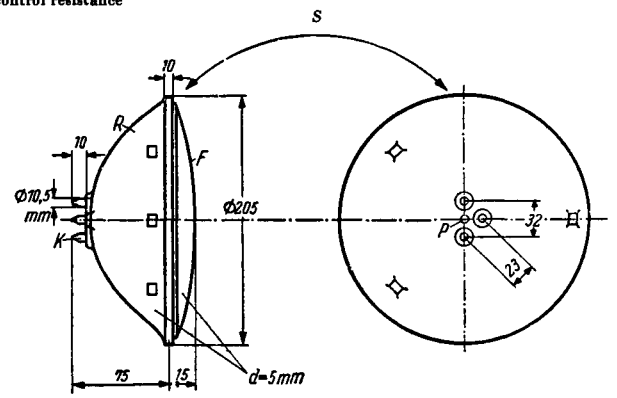


Fig. B 10-161A Mazda floodlight, so-called "airplane landing lamp" (24 V, 600 W) with metalized glass reflector *R*, and electrically welded front window *F* (made by GEC)

K Kovar caps; *P* pumping stem; *S* seam weld

A second method is discussed by [4]GUYER and [3]SHAW. The seam between the two glass pieces to be joined is painted with colloidal graphite to form a small strip, or a glass filler-rod coated in the same way is laid in the seam (Fig. B 10-162). Small equidistant gaps are made in the graphite path, for instance by scraping off material with a needle, so that the applied voltage produces a series of small arcs. Glass under the

arcs is heated and its resistance falls. At the same time, the conductor burns slowly back from the arc areas. These two effects, fall of resistance and increase of arc length, shift the passage of current from air-arc and graphite to glass as it heats. The advantage of the filler-rod is that it heats quickly to melting point without the other components being deformed.

Electrical resistance welding of glass in the manufacture of hard glass joints has the following advantages over the flame welding process:

(a) higher temperatures in shorter times;

(b) much less surface evaporation from the glass, as the heating is volumetric, not superficial; it is therefore specially suitable for thick-walled glass; [10.3]

(c) the weld zone can be restricted to a small area, and neighboring parts are not in danger of deformation;

(d) exact control of heating produces better and more homogeneous joints;

(e) unskilled personnel can be used whereas flame welding usually needs specialists.

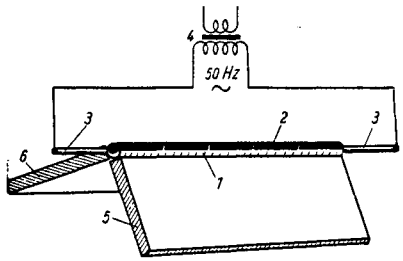


Fig. B 10-162 Welding glass seam with filler rod coated with strip of graphite ([2], [3]SHAW)

1 solid glass filler rod, cylindrical; *2* interrupted graphite strip, painted on and resistance increased by discontinuities; *3* leads; *4* H.V. source, 50 c/s (cf. Fig. B 10-161); *5* and *6* hard glass plates, to be edge-welded

10.3.VI. *Other Processes of Thermoplastic Glass-working*

Dielectric heating, and softening, of glass in the UHF field of a capacitor is possible but has so far only been used for laboratory investigations ([3]GUYER).

See Chapter 31 for melting of very high softening-point glass, especially quartz, with Ta foil in the hot atmosphere of a magnetically blown electric arc.

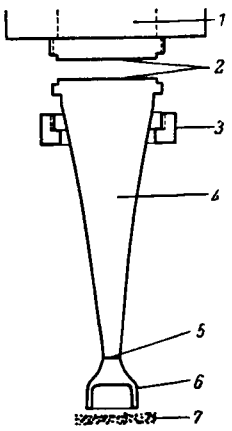
10.3.VII. *Mechanical Methods of Glass-working*

Turning and milling and similar processes can be applied to glass by using carbide tools (see, e.g., FEHSE, LUDWIG), but are seldom used in HV technique. Glass plugs, and flat or dished presses (Fig. B 10-137) with holes for lead-throughs are mostly ready-cast, pressed, or ground at the glassworks and are supplied by them.

WOYTACEK discusses preparation of ground-glass joints by aqueous suspensions of SiC on a lathe. The internal grinder is a conical rod and the outer an Fe or Cu tube, carrying the grinding fluid. See Chapter 29 for sizes and shapes of circular specimens, particularly the plug sections of stopcocks. Rough grinding of glass (e.g. removal of cast-ends of a large press to make tubular openings, Fig. B 10-137) is best carried out by carbide wheels with a water-spray coolant, or on a slowly revolving iron lap with SiC powder and water. The rough surfaces so made are often given a high polish by the methods standard in the optical industry; Fig. B 10-137 shows an example.

Small holes in glass can be made with a triangular carbide drill under turpentine. Large ones are best made with SiC powder in water and a slowly rotating Cu tube of the same diameter as the hole to be ground; the tube-end is notched to provide working

[10.3]



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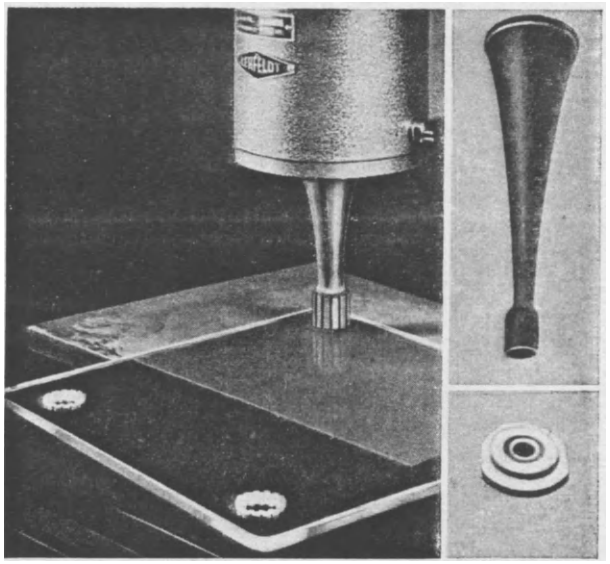

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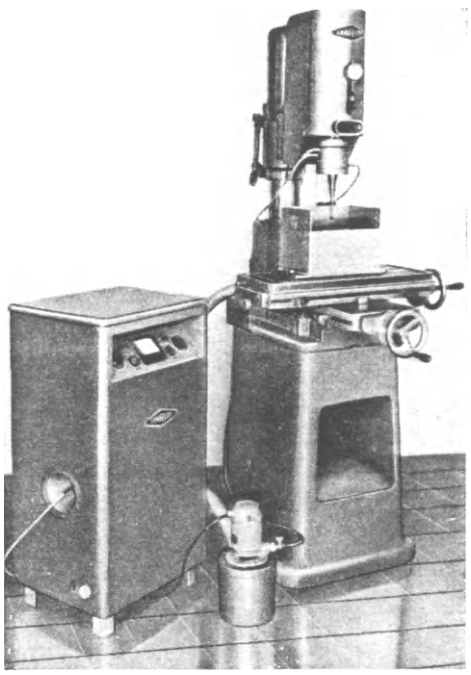


III

Fig. B 10-162A Ultrasonic drill for making holes of any desired profile to $\pm$ 0.01 mm in brittle materials like glass or ceramic (courtesy of Dr LEHFELDT UND Co., Heppenheim/Bergstraße (cf. also Fig. B 12-10D)

I diagram of drilling head: *1* oscillator; *2* plane parallel abutment with grease interlayer; *3* cap screw; *4* tough tool steel drill-stem; *5* brazed joint; *6* U/S drill-tip of unhardened tool steel (see also Fig. B 12-10D); *7* aqueous suspension of B_4C powder. II photograph of drill-head with work samples of glass and ceramic. III view of complete unit, type "Diatron" (left: U/S generator, 22 kc/s, 400 W max. U/S power; bottom centre: circulating pump for cutting fluid; right: drill-press)

space for the grinding agent (STEYSKAL). Any low-melting cement will fix the work to a metal backing, e.g., 2 parts resin, 1 wax of M.P. about 70°. Safety glass and breathing filters should always be worn when grinding glass, especially with grinding wheels.

A recent method for working glass, ceramics (Fig. B 12-10D), gemstones, and carbides is ultrasonic technique, especially for drilling of holes of any desired profile. Very fine grains of a grinding agent, generally B_4C, are vibrated by a tool (Fig. B 10-162A) excited at ultrasonic frequencies; this chips out the contour of the tool in the work in a microscale operation (see, e.g., LEHFELDT, NEPPIRAS, [18]ANON.).

See 10.4.XVIII for chemical etching, and XIX and XX for chemical and electrolytic engraving of glass. [10.3]

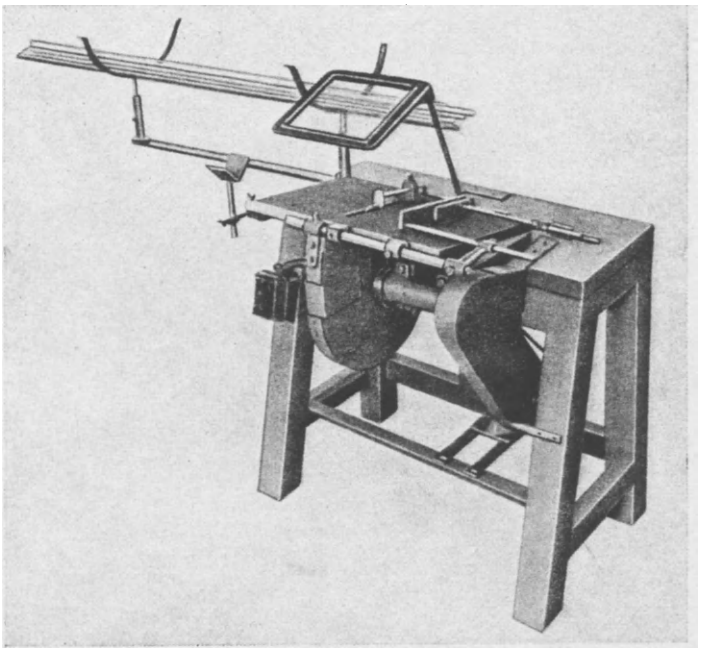


Fig. B 10-163 Cutting machine with steel slitting wheels and adjustable stop for hand cutting of as-supplied glass tubing (type S 2, made by AMBEG, Berlin-Schöneberg)

Cutting of glass. An important operation, which in mass-production of soft glass tubes can be very precise, is cutting off glass tube by stress or heat cracking. Various methods are available. The first way is to score the glass mechanically at the cut-off line with a diamond or a hardened steel or SiC wheel and then crack it off by applying a tensile or bending load. Figure B 10-163 shows a device for doing this. Sharp-edged slitting wheels spin at 2000 r.p.m. on the periphery; they run on ball-bearings to eliminate end-play so that a hairline scratch can be made in the glass. The unit shown in Fig. B 10-164 can be used for coarser work and larger tubes. Here, several glass tubes in channels are pushed against a stop by a rubber roller and the ends projecting beyond *K* are cut by a short blow from the knife *W* which is aligned with *K*. This can only be used for small-diameter tube and gives a rather jagged end.

The second method has long been used in hand glass-blowing for large diameters from 40 mm up, and also appears in automatic mass-production. This is local heat-cracking at a previously scratched line. Expansion strains are set up in the glass by

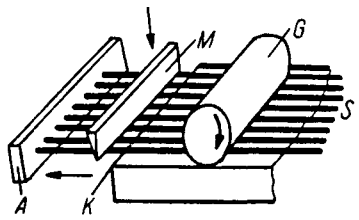
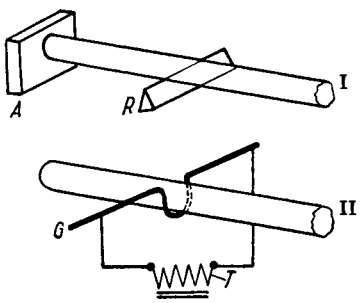
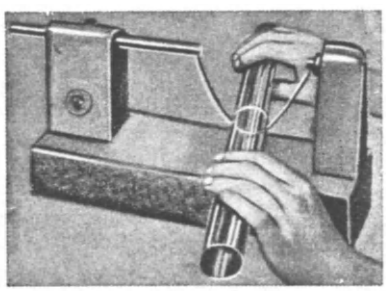


Fig. B 10-164 Simultaneously cutting several pieces of glass tubing with a breaking knife [10.3]

G rubber roller, feeding glass tubing *S* to stop; *A* stop; *M* breaking knife; *K* counter-edge for knife





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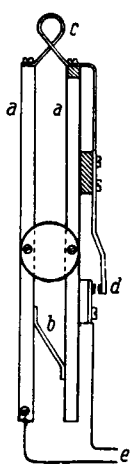

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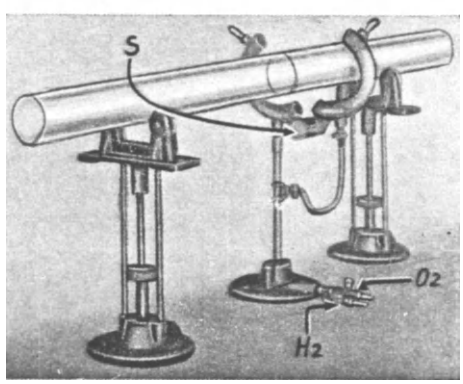


V

Fig. B 10-165 Cracking pre-scratched glass tube with hot wire or burner

I scratching process: *R* scratch knife (SiC); *A* stop
II cracking by sudden local heating of scratch by hot wire *G* heated by transformer *T*
III production model by EISLER ENG. Co.
IV hot-wire "pliers" for cracking large-diameter tube (MÖBIUS): *a* metal strips; *b* compression spring; *c* FeCr hot-wire loop; *d* hand-switch for current supply; *e* leads to 6–11 V transformer
V production model of crack-off ring burner, made for 25–350 mm dia. tube, burning oxyhydrogen or gas-air mixtures; *S* hinge joint for opening burner ring (made by EISLER ENG. Co.)

heating on one side, and these lead to fracture when the tensile strength is exceeded at some point. Cracks result, always along the weakest line, and therefore along the scratch. Local heating by hand methods involves contacting the scratched surface with a pencil-point of hot glass or applying a length of wire bent to fit the tube and pre-heated in a torch to red-heat. For larger numbers one can use electrically heated wires or very small, very hot flames of H_2. Figure B 10-165 shows simple crack-off devices of this type. The basic requirement for crack-off is thermal gradients in the tube wall and thus mechanical stress, so it can be seen that thin-walled soft glass and hard glasses of low α are much harder to crack-off than thick-walled soft glass. Quartz glass has so low an α [10.3] that it cannot usually be cracked by local heating (see Chapter 11). Hard glass can be

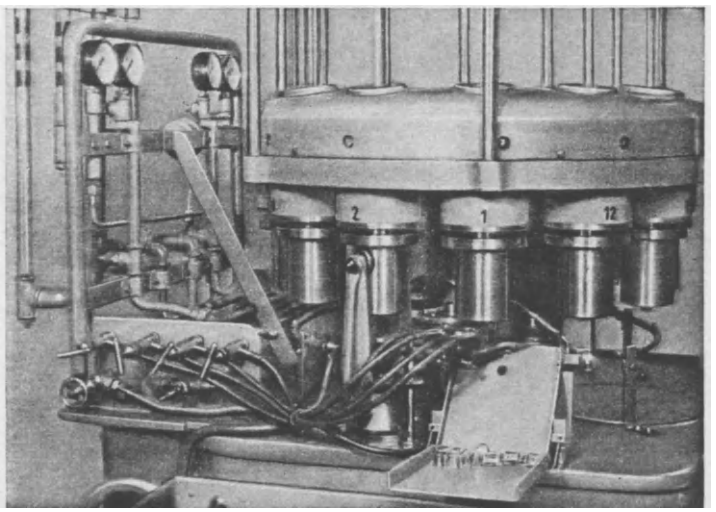


Fig. B 10-166 Double automatic machine for cracking glass rings from the "rod" (tube) with oxyhydrogen flames and water-cooled Cu crack-off disks (type OP, made by ELSTROJ-Prague)

Glass dia. 4–26 mm; glass lengths 5–20 mm; output 700–2000 rings/hr according to diameter; rings used for making pressed flat bases as shown in Fig. B 10-134

most cleanly cut by deep-notching with a high-speed sharp-edged Al_2O_3 or SiC slitting wheel, when local heating will crack the glass. Also, thin high-speed steel disks are recommended for this (STEYSKAL), since no wheel particles can be left on the glass which may cause trouble in further working. The same considerations apply to glass tube with residual strains due to poor annealing; superposition of artificial strains and local, uncontrolled strain areas will produce uncontrolled cracks where not expected. See TRIER for temperature and stress ratios in cracking of glass.

There is a third method that has proved very successful in mass-production of short glass rings for soft-glass, flat presses; see Fig. B 10-134, 2 and 3. The glass tube, at room temperature, rotates and is contacted by a sharp oxyhydrogen flame; immediately after this a water-cooled rotating Cu disk touches the same spot on the tube. Continuous cut-off of very short glass rings from the tube is possible by this method provided that, before each new cut, the end of the glass tube heated by the previous step is allowed to

cool sufficiently. The automatic turntable machines of Figs. B 10-166 and B 10-166A take care of this by turning the tubes continuously and moving them through five

[10.3]

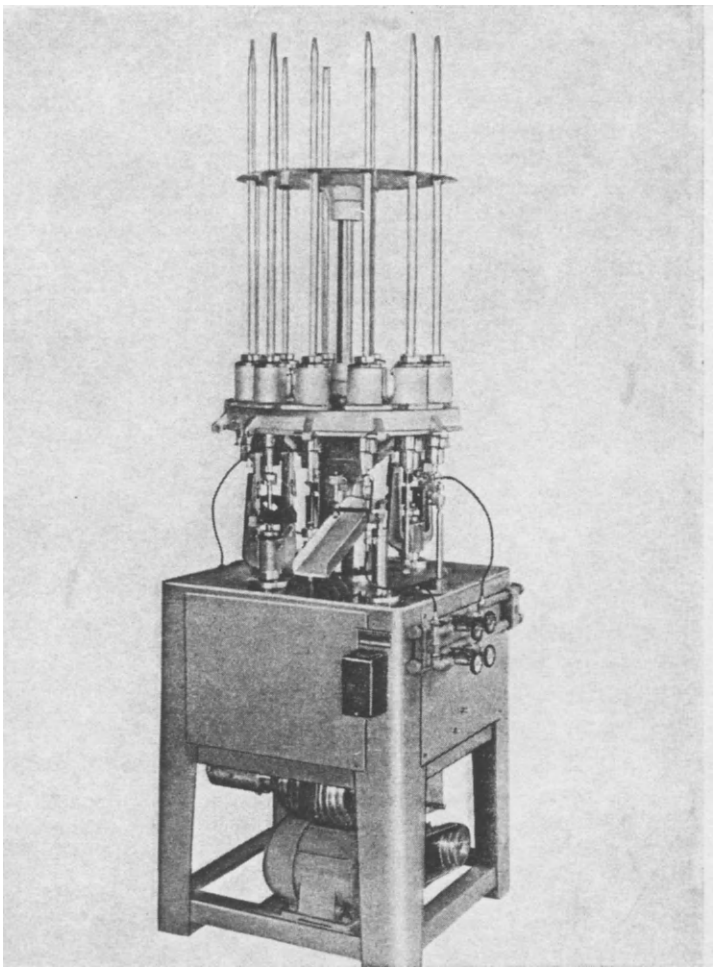


Fig. B 10-166A Automatic glass tube cutting machine with 12 positions (dual model) for cracking glass rings from the "rod" (type GLA 12, made by SCHMIDT UND KLEINBERG, Neu-Ulm/Donau)

Glass dia. 5–21 mm; glass lengths 10–50 mm. An O_2–H_2 flame from a special burner heats the cut-off zone, and two rings are cut at once by automatic water-cooled disks; the tube lengths are moved on to the next position and lightly flame polished at the edges. Output 1600–2000/hr

empty positions between cut-off points before flaming and cracking-off in the last positions. The machines illustrated work on a dual basis with 2 crack-off and 2×5 cooling positions and can produce 700–2000 rings, according to diameter, in lengths from 5 to 20 mm and 24 down to 4 mm dia.

Figure B 10-167 shows a machine of high output for cutting greater lengths, as are needed for making cylinder envelopes of miniature tubes of the type in Fig. B 10-148. Diameters between 6.5 and 23 mm in lengths of 45–190 mm can be made at the rate of 6000–9000 hours.

It is important to flame-polish the edges of cut sections for making tubes or envelopes before further glass-working on automatic machines. In mass-production, this is often done in the final position on the crack-off machine.

[10.3]

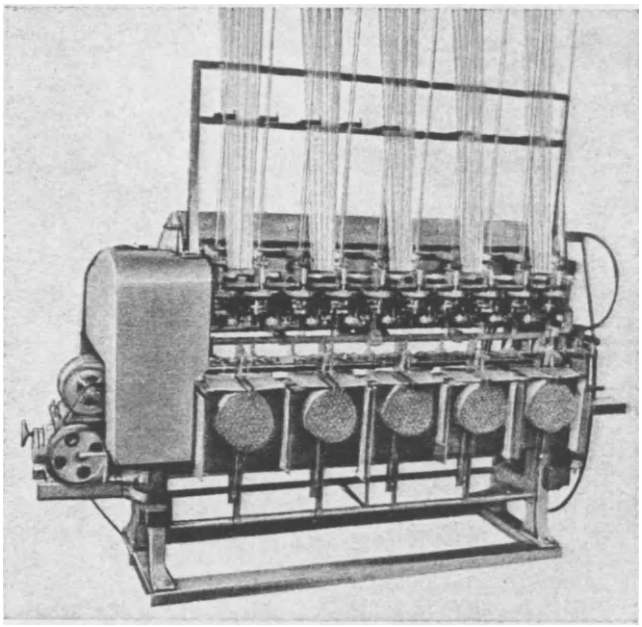


Fig. B 10-167 Glass tube cracking machine employing hot-and-cold process to make glass rings of 45 to 190 mm length and dia. 6.5–23 mm (type AS, by AMBEG, Berlin-Schöneberg)
Output: 6000–9000/hr, varying with diameter

10.3.VIII. *Annealing of Worked Glass*

(ADAMS, DAUVALTER, ENDELL, MURGATROYD, [2]SPÄTE, [1]THOMAS)

In all glass-working processes, fracture must be prevented by careful avoidance of internal strains, which can lead to damage, often only after prolonged storage and use, and especially under additional mechanical and thermal stress.

Stresses can arise from various causes:

1. inadequate matching of expansion characteristics of metal and glass in seals, see Chapter 30;
2. too large a difference between expansion coefficients of two glasses joined together;
3. annealing too rapid and uneven, leading to compressive and tensile stresses between the quickly chilled outer skin and the core which cools later.

The first two sources of stress can only be removed by suitable choice of materials and perhaps constructional measures; tempering will remove tensile or compressive stress caused by cooling. In glass-metal seals, there is also a special process called "differential annealing", in which glass and metal are deliberately held at different temperatures in the transformation range of the glass (see Chapter 30 on vacuum-tight glass-metal seals).

Tempering is especially important for all thick pieces worked by flame in high-speed machines; this applies particularly to pinch-and-press-feet, and often also to hand
[10.3] glasswork of complex design which experience has shown always exhibit rather high stresses after thermoplastic forming, due to relatively fast and uneven cooling. In order to anneal them, such pieces are taken immediately after working and where possible without letting them cool right down, and either held at or reheated to temperature for long enough to stress-relieve them sufficiently but without causing deformation from over-softening. They are then slowly and evenly cooled so that no further strains can be set up. The success of tempering depends strongly on programming, i.e. the rate of rise, dwell-time and fall rate of temperature in the furnace. Since stress-relieving is not possible in any practical time-interval once below the annealing point (see 10.2.II, 15 minutes stress-relieving point), to correctly temper glass it must be held for enough time at least 5° above this point. Roughly, the rate of stress-relief doubles, so the time needed is halved, for a 7–9° rise in annealing temperature (MURGATROYD). Temperature programs are obviously determined by shape and size of the work, in hollow-ware mainly by wall-thickness, and in all cases primarily by the type of glass, since, other things being equal, the stresses are higher the greater the expansion coefficient.

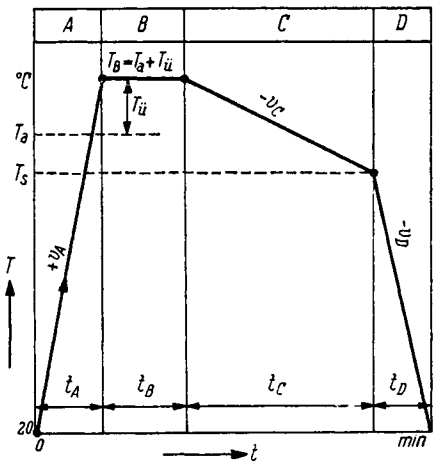
10.3.VIII*a*. *Practical Tempering Programs*

REDSTON has set up procedures for calculating a relatively simple temperature time program, as shown in Fig. B 10-168. Graph I sketches out the basic tempering program. The individual parameters can be obtained from graphs II–V as follows:

First, the group of lines II serves to determine the maximum cooling rate v_C for stress-relieving for glass of maximum thickness d and expansion coefficient α, in °C/min. This is the rate to be adhered to when traversing the temperature range C between annealing temperature T_B and strain temperature T_s. One can allow a cooling rate which produces stress in the center of the work corresponding to a path (phase) difference of 2.5 mμ/cm as measured by polarization microscope. As can be seen from II, v_C is higher the smaller the expansion coefficient and the thinner the wall of the glasswork. For the given v_C, III is used to fix a so-called "excess temperature" $T_{\ddot{u}}$ from which the annealing temperature $T_B = T_a + T_{\ddot{u}}$ is found. T_a is the glass annealing temperature ($\eta = 10^{13}$ P approx.) As can be seen, $T_{\ddot{u}}$ can be negative. IV then gives the "holding time" t_B, i.e. the annealing time-interval corresponding to $T_{\ddot{u}}$, and the work must be held at constant T_B for this long before cooling to the strain temperature T_s at rate v_C. Once below T_s, the work can be very rapidly cooled at rate v_D which is obtained from diagram Va and Vb (CORNING data) for various thicknesses and expansions. If T_s is not known, the work should be cooled to 100° below the annealing temperature T_a. The heating rate v_A to which one can subject the work when raising it to T_B and which is quite rapid,

equals v_D; so that now all parameters for the program of Fig. B 10-168$_1$, I, are determined.

Figure B 10-169 gives a somewhat more complex temperature time schedule based on CORNING Glass Works data. It has five stages, not four as in the REDSTON program [10.3]



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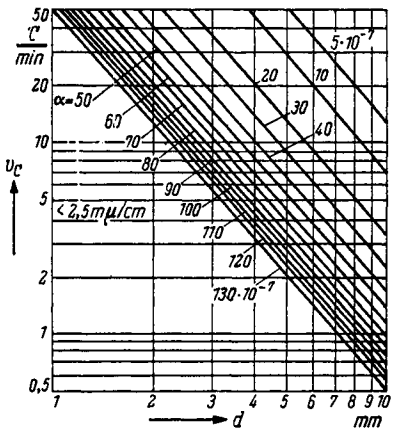

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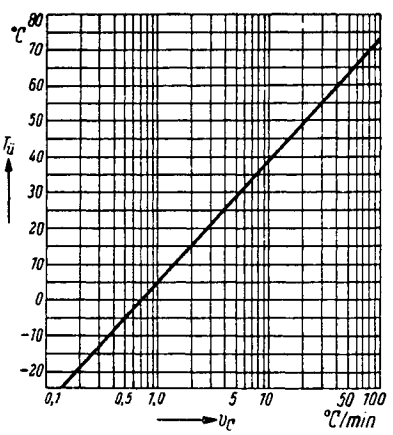
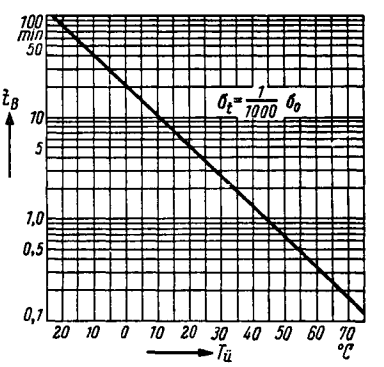


III



IV

Fig. B 10-168$_1$ Graphs for determining a temperature-time program for annealing small glass parts such as lamps, seal-ins, press-feet, envelopes and pressings (REDSTON)

I the overall T–t annealing process: A heating; B anneal; C even cooling; D chilling

II cooling rate v_C for various thicknesses d and expansion coefficients α of glass (permissible stress after annealing: 2.5 mμ/cm in center of body)

III optimal excess $T_ü$ for various cooling rates v_C

IV annealing time t_B as a function of excess temperature $T_ü$ (residual stress after relieving, $^1/_{1000}$ of initial)

of Fig. B 10-168, I, and this is because it differs by having two stages of homogeneous cooling after annealing, each with its own rate, v_C and v_D. The parameters for the CORNING scheme for various expansions and thicknesses are given in Table T 10–21, both for one-sided cooling (e.g. for small-bore tube of wall d) and for two-sided cooling (e.g. for

[10.3]

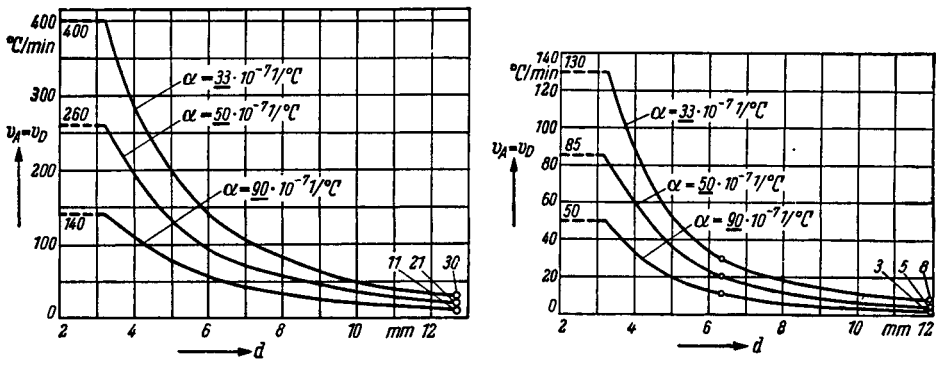


Fig. B 10-168$_2$ Graphs for determining a temperature-time program for annealing small glass parts such as lamps, seal-ins, press-feet, envelopes and pressings (REDSTON)

V heating and cooling rates v_A and v_D as functions of thickness d of the work for various expansion coefficients α of the glass ([1]CORNING)

Va curves for heating and cooling on *two* sides

Vb curves for heating and cooling on *one* side

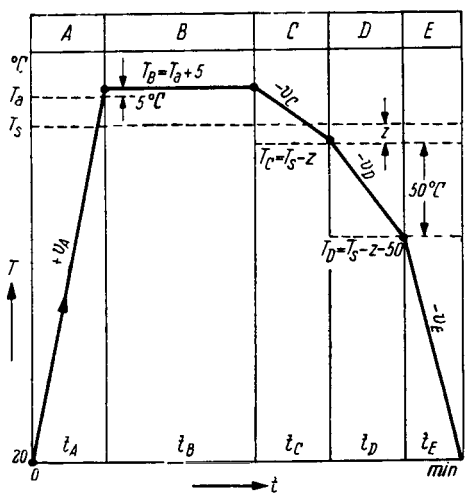


Fig. B 10-169 Temperature-time (T-t) annealing program used by CORNING

A heating; *B* annealing; *C* first homogeneous cooling; *D* second homogeneous cooling; *E* rapid chilling. Parameters from Table T 10–21

flat press of thickness d or solid rod of dia. d). The table refers to *commercial* glassware, where the residual strains have to be reduced to a reasonably low value and that is all that is required. *Optical* glass, which can have at most such strains as correspond to a path (phase) difference of 10 mμ/cm in order to maintain a constant refractive index, require a so-called "fine annealing", details of which are given by [4]LILLIE.

A graphical comparison of the REDSTON and the CORNING programs is given in Fig. B 10-170. As can be seen, the overall times are rather similar.

10.3.VIII*b*. *Tempering Furnaces*

We now consider the practical process of tempering and the first point is that a pre-tempering is often carried out by the glass-working machine, especially when the glass-work runs through a series of "annealing flames" after forming on the machine. However, one can limit the annealing process to this pre-tempering only when the glasswork [10.3]

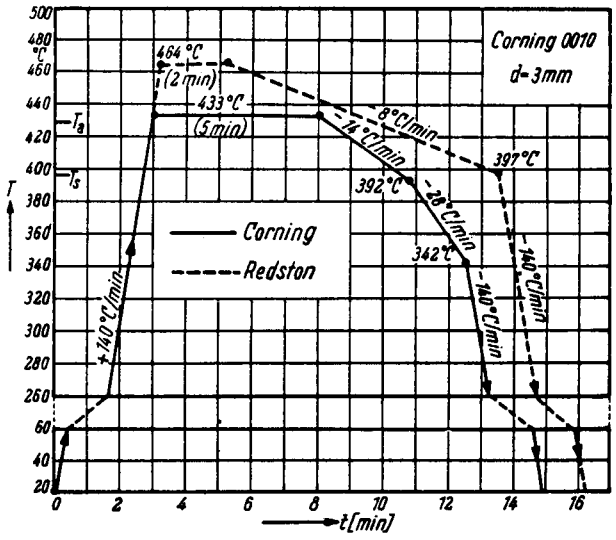


Fig. B 10-170 Comparison of CORNING (———) and REDSTON (— — —) annealing programs for dished press-foot 3 mm thick of Corning Pb-glass 0010 ($\alpha = 91 \times 10^{-7}$ 1/°C; $T_s = 397°$; $T_a = 428°$)

will have very low mechanical stresses applied to it, or when the product will undergo a thorough tempering after joining to another piece of glasswork.

Tempering proper takes place in special ovens that can be subdivided by their construction into three main groups: rotary, conveyor and chamber kilns. Examples of the first two are given in Figs. B 10-171 and B 10-172; the completed glasswork travels from the machine into the kiln, through which it passes; it is then fed automatically down a slipway or is placed by hand in the kiln, which is gas or electrically fired. To achieve the most even temperature distribution, all tempering furnaces are provided with sheet Cu inserts, grog and asbestos lining, double-wall insulation, light-colored outer coating, etc. Very large closed furnaces have the air agitated by fans. Glasswork of large thermal capacity can be tempered without further heating, under certain conditions. Immediately forming is finished, the glass is still above the annealing temperature so that no strains can be set up; it is then placed in a pre-heated annealing pot or jar with asbestos lining where it is left to self-anneal evenly by slow decay of its own stored heat for the desired time. It is often the case, especially with thick-walled parts, that at the time of insertion in the annealing oven there are already local areas below

annealing temperature, where fairly high stresses will have formed. It is often sufficient here to leave the work in insulated annealing pots to equilibrate thermally to the desired homogeneous annealing temperature.

The larger tempering ovens should be provided with temperature measuring and control devices. Since the 15 minutes stress-relieving temperature, even for hard glass, is not much higher than 600°, Hg-switch thermometers or thermels can be used to indicate temperature. For control purposes, the more precise temperature-drop bow-type controller or thyratron controller is best. By installing a programming disk, it is pos-

[10.3]

TABLE T 10-21. THE CORNING TEMPERATURE-TIME PROGRAM FOR ANNEALING COMMERCIAL GLASSES (CF. FIG. B 10-169)

TIME INTERVAL	OPERATION
t_A	Heating to 5° C above annealing point T_a
t_B	Annealing at $(T_a + 5)$° C
t_C	First homogeneous cooling to z° C below strain point T_s at rate v_C
t_D	Second homogeneous cooling for further 50° C at rate v_D
t_E	Final cooling to room temp. at rate v_E

Time and temperature data:

		Range A	B	C		D	E
EXPANSION COEFFICIENT α (1/°C)	GLASS THICKNESS d (mm)	HEATING RATE v_A (°C min)	ANNEALING TIME t_B (min)	TEMPERATURE z (°C)	COOLING RATE v_C (°C/min)	COOLING RATE v_D (°C/min)	COOLING RATE v_E (°C/min)
		For one-sided cooling					
33×10^{-7}	3.2	130	5	5	12	24	130
	6.3	30	15	10	3	6	30
	12.7	8	30	20	0.8	1.6	8
50×10^{-7}	3.2	85	5	5	8	16	85
	6.3	21	15	10	2	4	21
	12.7	5	30	20	0.5	1.0	5
90×10^{-7}	3.2	50	5	5	4	8	50
	6.3	11	15	10	1	2	11
	12.7	3	30	20	0.3	0.6	3
		For two-sided cooling					
33×10^{-7}	3.2	400	5	5	39	78	400
	6.3	130	15	10	12	24	130
	12.7	30	30	20	3	6	30
50×10^{-7}	3.2	260	5	5	26	52	260
	6.3	85	15	10	8	16	85
	12.7	21	30	20	2	4	21
90×10^{-7}	3.2	140	5	5	14	28	140
	6.3	50	15	10	4	8	50
	12.7	11	30	20	1	2	11

sible to control the temperature cycle automatically so that it follows a course like that of Fig. B 10-170. The large degassing furnace for TV-tube pumping-lines (Fig. B 10-250) can obviously also be used for annealing.

10.3.VIIIc. *Tempering by Radiant Burner*

It is very difficult to provide rapid and homogeneous heating of glassware with varying wall-thickness, such as TV tubes with thick picture panel and relatively thin cones,

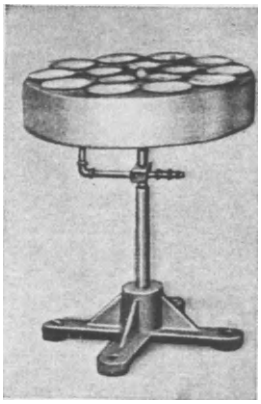


Fig. B 10-171 Rotary oven for annealing and gradual cooling of small vacuum-tube envelopes after sealing in the foot (made by GLADITZ, Schwäbisch Gmünd/Württemberg)

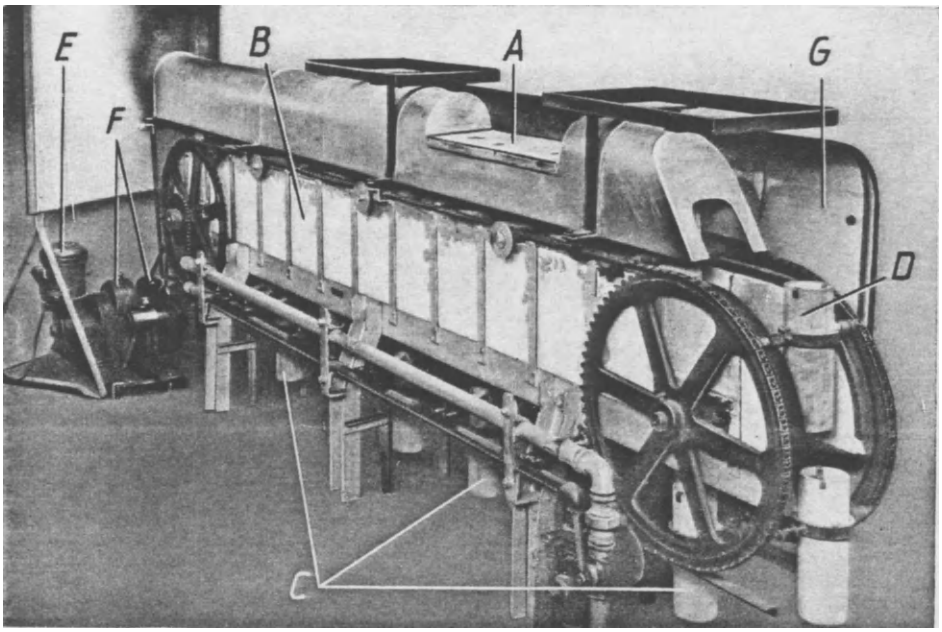


Fig. B 10-172 Gas-heated conveyor oven with stepwise belt drive for tempering large glasswork ([5]ESPE)

A input opening with coverplate; *B* oven with stage-wise decreasing firing; *C* feedback of work outside oven (the work is placed in metal containers of large thermal capacity and cools slowly); *D* removal of tempered work; *E* drive motor; *F* drive, dog wheel and Maltese cross; *G* double-walled asbestos lagging, front section removed

if the work is heated directly in the flame. For this reason, industry has developed radiant gas burners (BURDETT, HOLZBECHER, LE MAY, RAVIČ, [2]RICHARDSON). Figure B 10-173 shows the principle and Fig. B 10-174 shows the detailed components and construction of some production models. A compressed air + gas mixture is burnt to completion in the burner and thereby heats a sintered ZrO_2 surface to about 1300–1500°; this surface now radiates intensely with an energy maximum at about 1.4 μ (Fig. B 10-175), but the flame does not extend beyond the opening of the burner. Figure B 10-176 shows a flat model, the so-called "diaphragm burner", where the gas + air mixture is fed
[10.3] from a chamber through a ceramic diaphragm and burns at the top surface of the latter as many small non-luminous flames, which raises the ceramic surface to a "flameless" incandescence. To prevent combustion inside the capillaries, the gas-air flow-rate must obviously be higher than its combustion rate. For further details see HOLZBECHER.

The radiant gas burner has a series of advantages over the flame burner:

(a) no combustion gases or carbon deposits reach the work;

(b) if the work is made of ordinary glass of relatively good transparency to thermal radiation, its volume is heated by absorption of radiation alone rather than by unilateral heating of the surface and thermal conduction inwards. Since unilateral radiation will heat both sides of the glass, short heating times can be achieved without danger of fracture;

(c) radiation burners can be made directional; as a result it is possible, for example, in a traveling-grate tunnel kiln without partitions to produce temperature distributions which would be hard to achieve in electrically-heated furnaces.

(d) tempering furnaces with radiant gas burners are much cheaper and more efficient than the corresponding resistance-heated furnaces.

Figure B 10-177 gives an example of an annealing and sintering furnace fired by diaphragm-type radiant gas burner; it contains glass tubes for low-pressure Hg-vapour fluorescent lamps up to 1.5 m long and coated internally with phosphor powder, which rotate continuously at the M_g point (see Table T 10–5). The usual luminous-tube glass M_g point is *ca.* 530° (KRATOCHVÍL). This single process anneals and corrects them, and at the same time the phosphor is fired on to the glass wall, the binder in the phosphor is evaporated off, and the paraxial conducting coating used for striking the tube is sintered on; this coating is generally applied as a suspension of metal powder on the outside of the tube (Figs. B 10-231 and B 10-232). Figure B 10-178 shows a large conveyor furnace with gas-fired radiation burners of the type in Figs. B 10-173 and B 10-174; this furnace is for annealing TV tubes, and also for baking on the fluorescent screen and the internal graphite layer.

In all tube-annealing processes where the electrode system including parts made of air-sensitive materials is already mounted, protective gas flushing is recommended (such as with dry N_2 or CO_2) at a flow of about 10 liters/hour until the tube has cooled to at least 200°.

10.3.IX. *Measurement of Strains in Glass*

To satisfy oneself of the absence of strains in glasswork, or to establish their presence, it is necessary to have at least a qualitative method of indication, and to evaluate new materials and processes quantitative measurements are required. This is possible because

tensile or compressive stresses in transparent glass give rise to double refraction, proportional to the stress, which can be seen with the aid of polarization equipment. A short exposition of the basis of measurement follows; more detail is given by BARTELS, HAAS, HETÉNYI, HONIGMANN, MESSMER, PADMOS, PARTRIDGE, A. F. ROGERS, [2]SPÄTE.

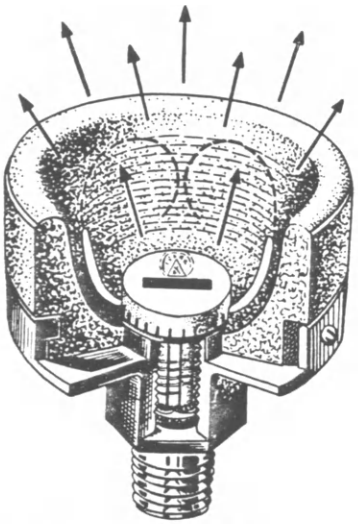
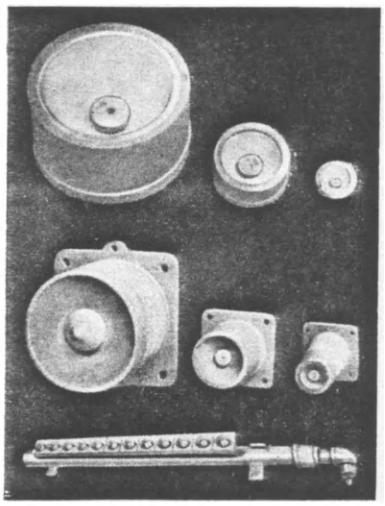


Fig. B 10-173 Construction of gas-heated radiation burner, so-called "bowl burner"
Gas + air mixture leaves the side holes of the burner with complete combustion inside the ceramic pot and heats the inner wall to over 1300° (made by SELAS CORP. of America, Philadelphia)



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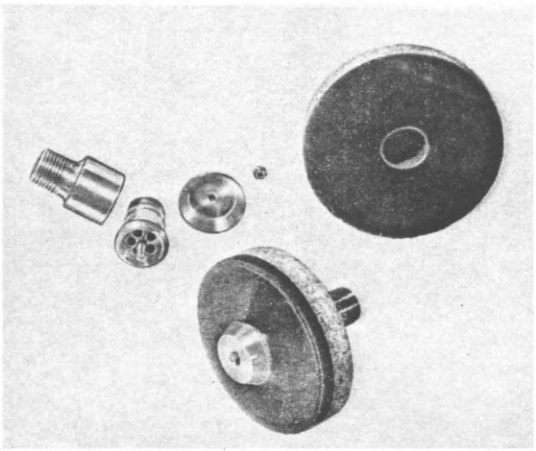
[10.3]



II

Fig. B 10-174 Components and construction of radiant gas burners
I American types (from LE MAY)
II European types (from [2]KRATOCHVÍL)

Annealed homogeneous glass is physically isotropic: thermal and other properties are invariant under change of axis and an incident light-ray is singly refracted according

to the well-known law and is propagated in every direction in the glass with equal velocity. However, if glass is strained it is anisotropic, i.e. exhibits different properties in different directions; an incident ray is doubly refracted by an optically anisotropic crystal, i.e. two rays are formed, the ordinary and the extraordinary rays, which are

[10.3]

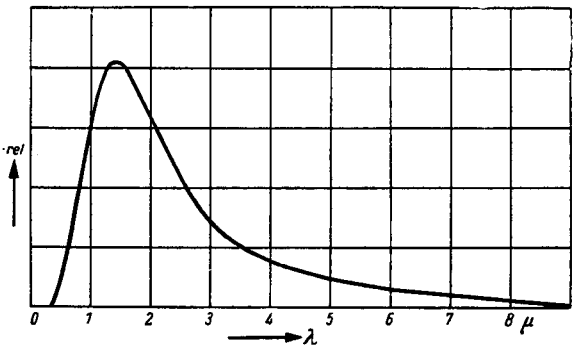


Fig. B 10-175 Spectral distribution of thermal radiation from a gas-fired SELAS burner of the type shown in Fig. B 10-173

polarized in two mutually perpendicular planes, one ray traveling along the optical axis, and the rays are propagated at different velocities through the glass. For example, if a homogeneous, annealed cube of glass is subjected to an even stress-distribution of either sign over the whole of two opposite surfaces, it behaves as a monaxial crystal,

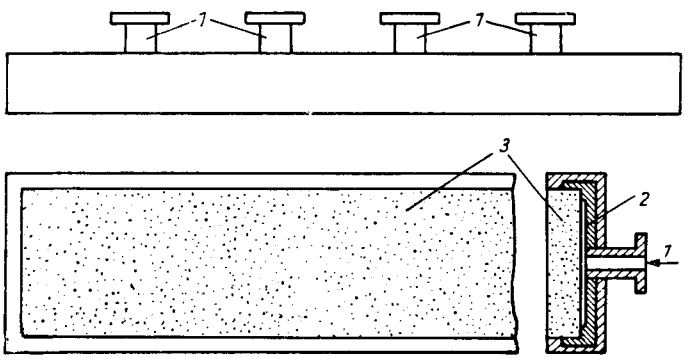


Fig. B 10-176 Design of a diaphragm-type radiation burner ([2]KRATOCHVÍL) (made by RADIANT HEATING LTD., Barnsbury Park, London)

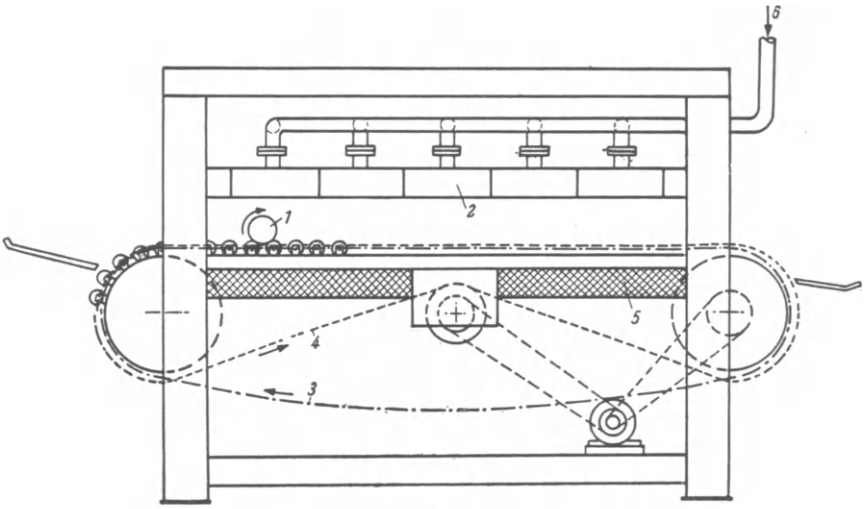
The gas + air mixture is fed via line *1* into chamber *2* and thence through diaphragm *3*. It burns as many small non-luminous flames at the surface of *3*, which is thus raised to uniform incandescence

optically speaking, with the axis lying in the direction of the stress vector. The ray whose polarization is parallel to compression has a higher velocity of propagation than that of the other ray, and vice versa for tension. The result is that one ray is delayed with respect to the other so that there is path difference Δ caused by traveling through the

glass, and this is proportional to the thickness of the glass traversed and the prevailing tensile or compressive stress, i.e.

$$\Delta = C \cdot d \cdot S,$$

where Δ (usually measured in $m\mu = 10^{-7}$ cm) is the path difference, d (cm) the glass [10.3]



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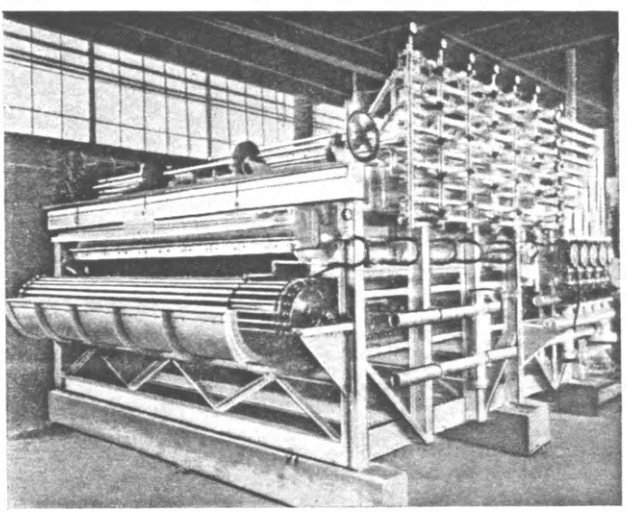


II

Fig. B 10-177$_1$ Annealing and sintering conveyor furnaces for fluorescent lamp tubes up to 1.5 m long. Heating is by radiant gas burners from above ([2]KRATOCHVÍL, [2]RICHARDSON)

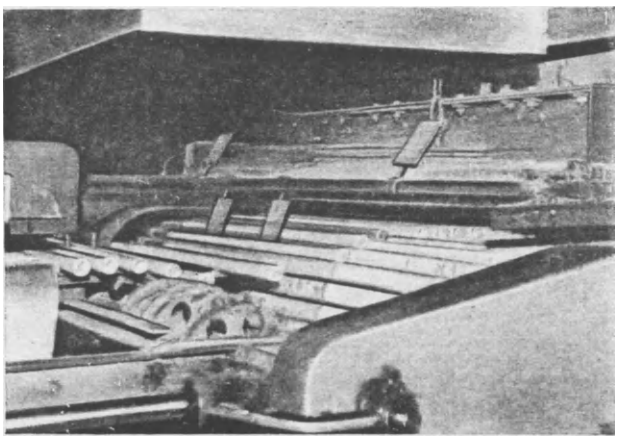
I construction: *1* glass tube; *2* diaphragm burner; *3* chain drive for feedof transport rollers; *4* chain drive to rotate transport rollers as they travel; *5* fire-clay lining; *6* gas + air line

II overall view of production equipment (cf. LE MAY)

thickness, S (kg weight/cm²) is the load, and C is a proportionality constant $\left(\frac{m\mu}{cm} \Big/ \frac{kg}{cm^2}\right)$ called the photoelastic constant, in BREWSTER units, which varies with the glass. See BALMFORTH for discussion of systematic measurements of the dependence of C on glass composition. The equation gives the path difference in mμ produced by a cube of glass 1 cm thick if its upper surface is loaded by 1 kg weight. One can also define the BREWSTER as follows: if a one-dimensional tensile or compressive load of 100 g (1 kg/cm²) is applied to a plane-parallel plate 1 mm thick and 10 mm wide normal to the direction of the test-ray of an optical strain-measuring instrument, the photoelastic constant of the material is 1 BREWSTER if the measured path difference is 1 Å. The unit C so defined

[10.3]

$$1 \text{ Brewster} = \frac{\text{Å}}{\text{mm}} \Big/ \frac{\text{kg}}{\text{cm}^2} = 1 \frac{\text{m}\mu}{\text{cm}} \Big/ \frac{\text{kg}}{\text{cm}^2} = 100 \frac{\text{m}\mu}{\text{cm}} \Big/ \frac{\text{kg}}{\text{mm}^2}.$$



III

Fig. B 10-177$_2$ Annealing and sintering furnace for glass tubes up to 1.5 m long for fluorescent lamps. Heated by gas-fired radiant burners from above
III exit end of the furnace (cf. LE MAY)

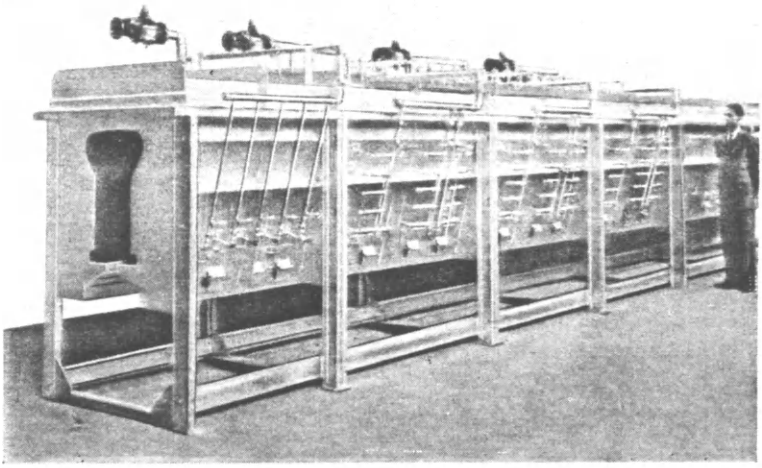
varies for various glasses between 2 Brewster for 80% Pb-glass and 4.5 for Pb-free glass, and for most technical glasses amounts to about 3 (Table T 10–22).

The determination of stress in a glass body, $S = C^{-1} \cdot \Delta/d$, requires not only a knowledge of the photoelastic constant C, but also the thickness and a measurement of the above-mentioned path difference. For instance: suppose a piece of glass 0.6 cm thick shows a Δ of 300 mμ, then Δ/d is 500 mμ/cm; if $C = 3.6$ Brewster, the stress $S = 500/3.6 = 140$ kg/cm². If the permissible stress is set at $^1/_{18}$ to $^1/_{16}$ of the tensile strength of 600 kg/cm², and an average value of C is taken to be 3, the maximum permissible path difference per cm is $\Delta/d = C \cdot S = 3 \times 600/16$ to $3 \times 600/6 = 100$–300 mμ/cm. In the case of heavily stressed glass, Δ/d is only permitted to be 30, and for optical glass annealing should proceed till the value does not exceed 10 mμ/cm anywhere.

It should be noted, however, that, as with a birefringent crystal parallel to the optical axis, so with a strained glass body there is no birefringence visible in the direction of

stress and therefore no stresses can be determined. A further point here is that in practice normally-stressed glass is not homogeneously birefringent, but exhibits local birefringence of varying intensity. Since it is not possible experimentally to measure this property at individual points, photoelastic tests always yield an arithmetic average in the direction of observation concerned. In most cases, these results are satisfactory provided

[10.3]



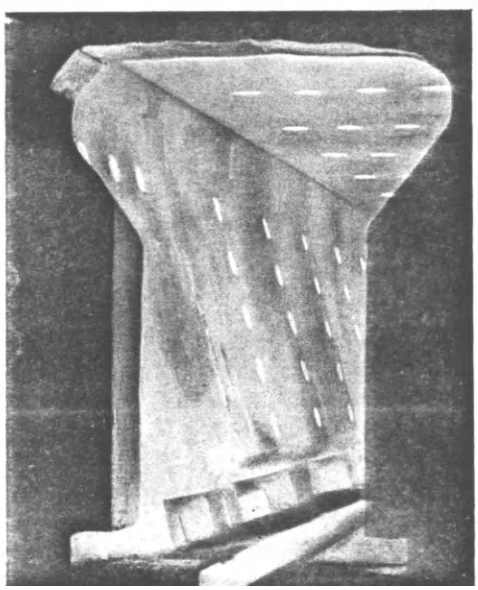


Fig. B 10-178 Construction of a large conveyor furnace with gas-heated radiant burners for annealing and baking of large TV tubes (LE MAY)

Below: view of the inside of the furnace during operation (cf. also Fig. B 15-52B)

TABLE T 10-22. PHOTOELASTIC CONSTANT C OF COMMERCIAL TECHNICAL GLASSES

TYPE OF GLASS	C (BREWSTER)[1]	TYPE OF GLASS	C (BREWSTER)[1]
CORNING		CHANCE BROTHERS	
0010	2.73	GH 1	3.56
0050	2.85	GS 1	3.82
		GS 3	4.26
0060	2.66	GS 4	3.55
		GS B	4.2
[10.3] 0080	2.39–2.47	GEN. EL. CO., WEMBLEY	
		B 8	2.68
0120	2.48	HH	3.54
		L 1	2.85
3320	3.47	W 1	3.56
		X 4	2.57
7050	3.6 (3.37–3.61)	X 8	2.55
		PHILIPS[2]	
7060	3.37	K 1a	2.8
		N 542	3.1
7070	4.36	ČSR-Glasses[2]	
7720	3.3 (3.29–3.40)	Fe-Glass	3.8
		Kovar (K 705)	4.0
		KS	2.8
7740	3.43	LL (K 707)	4.8
		M-Glass (Pb)	2.6
		Mg-Glass	2.6
7750	3.6	MoKa	3.1
		Palex	3.1
		PN	3.1
B.T.H.		Sial	3.2
C 9	3.64	Simax	3.1
C 19	3.60	Unihost	2.7
C 40	2.94	WoKa	3.3

(1) 1 BREWSTER $= 1 \frac{m\mu}{cm} \Big/ \frac{kg}{cm^2} = 100 \frac{m\mu}{cm} \Big/ \frac{kg}{mm^2} = 10^{-5} \frac{cm}{cm} \Big/ \frac{kg}{mm^2}$.

(2) SVOLF.

the glass body is rotated back and forth in the field of observation and the maxima recorded.

The measurement of path difference itself is carried out as follows (refer to Fig. B 10-179): a monochromatic light ray from source L with monochromatic filter F is linearly polarized by P in the direction R. The ray then passes through the strained glass body where as stated it is split into two polarized beams in mutually perpendicular directions R_1 and R_2, provided that the optical axis of the glass (the direction of stress) does not coincide with the direction of vibration of the polarized test ray (i.e. the plane of polarization of the polarizer P) or is normal to it. The best condition is when the plane of vibration makes an angle of 45° with that of the polarizer, that is, bisects the right angle between the polarization plane of the polarizer and that of the analyzer (see Fig. B 10-179). The two light rays now enter the analyzer A whose polarization plane is normal to that of P. Each ray is again split into two components along R_3 and R_4, and R_5 and R_6. The pair along R_4 and R_5 are not transmitted by A; the pair along R_3 and R_6 are transmitted with phase reversal so that they are brought into the same plane of polarization and produce interference corresponding to the path (phase) difference in the strained glass. This interference can include total extinction when the path difference is a multiple of the wavelength λ of the monochromatic ray, and maxi-

mum brightness is produced when Δ is an odd number of half wavelengths. This can be easily demonstrated by replacing the strained glass body by a birefringent optically-monaxial crystal of linearly increasing thickness, such as a crystalline quartz wedge, so that its optical axis makes an angle of 45° with the polarization planes of A and P (refer to Fig. B 10-180). If an unstrained glass body, such as a solid rod with a metal rod of equal thermal expansion sealed coaxially inside, is placed in the field of view of the wedge parallel to its optical axis, the dark lines (Fig. B 10-181, I) seen in the wedge are not altered in position (Fig. B 10-181, II). If, however, the glass rod exhibits axial strains due to expansion mismatch with the metal rod sealed to it, a path (phase) difference caused by birefringence in the glass is added or subtracted to that due to the quartz wedge and the dark lines are shifted up or down according to whether the stress is compressive or tensile (Fig. B 10-181, III). The shift is greater the higher the stress in the glass; it is easily found by photographic means or by measuring microscope and [10.3]

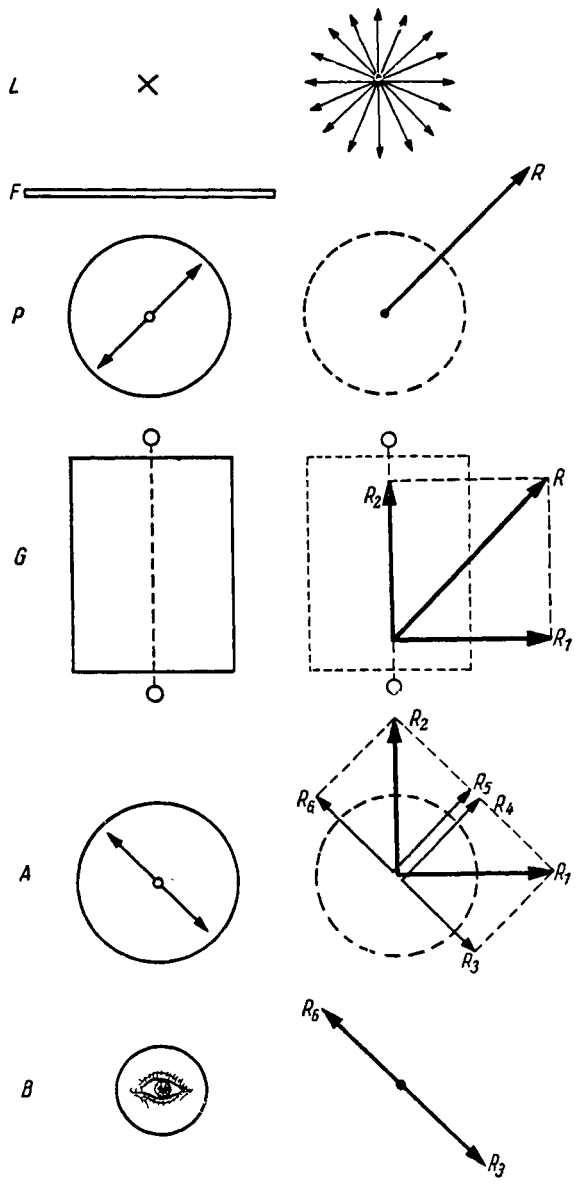


Fig. B 10-179 Principle of measurement of path or phase difference in strained glass

(All constructional elements of the polarization equipment shown on the left side, and the plane of polarization of the polarized test ray of light should be imagined to be normal to that of the paper.)

L light source with monochromatic filter F to produce test ray; P polarizer (direction of oscillation indicated by double arrow); G glass body under test (direction of stress ○ - - - ○, i.e. optical axis for best visibility is at 45° to direction of polarization of both polarizers); A analyzer, direction of polarization 90° from that of polarizer P ("crossed" polarizers); B observer (eye and ocular, photographic recorder or projector with ground-glass screen); R direction of polarization of original ray; R_1 to R_6, directions of polarization of split beams in test body and analyzer

equals the distance x in Fig. B 10-181, III. The interpretation of the direction of shift can be most easily settled and the shift is calibrated for stress by weight-loading (compressing) a well-annealed glass rod of the same size and type (Fig. B 10-181, IV, shift k corresponds to compression load $\sigma = G/Q$ (kg/mm^2)). The shift is towards the thin end of the quartz wedge for compressive axial loads, and to the thick end if tensile, provided the wedge is cut so that its optical axis is parallel to its long edge or side (Fig. B 10-181, V).

Figure B 10-182 shows an arrangement often used for glass–metal seals that works
[10.3] on the principles described. As is clear from the figure, glass test-bodies with strong curvature are best immersed in a tank made of strain-free plane parallel glass plates and filled with a fluid of the same refractive index as the glass, to avoid the troublesome refraction of light that takes place at the curved air-glass interfaces. The usual fluid is benzene (refractive index $n = 1.50$) or CCl_4 ($n = 1.46$) to which ethanol ($n = 1.36$) or

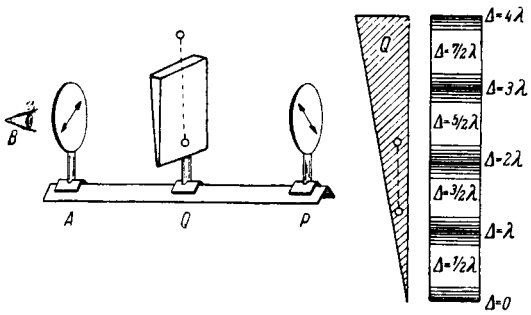


Fig. B 10-180 Interference pattern seen by inserting a crystalline quartz wedge Q between crossed polaroid filters (polarizer P and analyzer A); o— — —o is the optical axis of Q; B is the observer

CS_2 ($n = 1.63$) is added until the n of the glass (1.47–1.56, see Table T 10–4, A1) and of the fluid are sufficiently close, i.e. the contours of the glass surface disappear from the field of view. These fluids have high VPs at room temperature and thus cause discomfort to the observer (benzene: headaches, tinnitus; CS_2: poisonous); therefore large open tanks have other fluids like xylol ($n = 1.50$), tetralin ($n = 1.548$), monobromonaphthalene ($n = 1.66$), monochloronaphthalene ($n = 1.63$), chlorobenzene ($n = 1.53$) and other organic fluids of low VP, as far below 10 Torr as possible at room temperature. Obviously such an apparatus permits recording of strain patterns with an ordinary camera on photographic plates (see Fig. B 10-182A).

If the path or phase difference is measured in the polariscope, not with monochromatic but with "white" light—as in most high-quality technical apparatus—that is, with daylight or artificial light from a lamp, the destructive interference (discussed above) only occurs for certain wavelengths of the spectrum of white light. The complementary colors then appear in the field of view.

For example, suppose the value of Δ is 300 mμ, then extinction (minima) occur for $\lambda = 300$ mμ ($\Delta = \lambda$), 150 mμ ($\Delta = 2\lambda$), etc.; brightness peaks (maxima) occur for $\lambda = 600$ mμ ($\Delta = \lambda/2$), 200 mμ ($\Delta = 3\lambda/2$) and so on, that is, for Δ any integral multiple

of λ and for Δ any odd number of half wavelengths respectively. Of all these values of λ, only the maximum at 600 mμ falls in the visible range. Since this λ corresponds to yellow light, the field of view will appear yellow for Δ = 300 mμ. For values of Δ below 200 mμ one can calculate analogously that there will only be maxima and minima that are less than any λ in the visible. There is generally then no coloration but only a brightening of the field of view in grey plus a weak tint of blue-violet.

Only for large Δs above 400 mμ does destructive interference occur in the visible (i.e. minima). Suppose Δ is 565 mμ, then extinctions occur at λ = 565, 383, 188 mμ, and maxima at 1130, 377 and 226 mμ. This means that the yellow-green λ of 565 mμ drops [10.3]

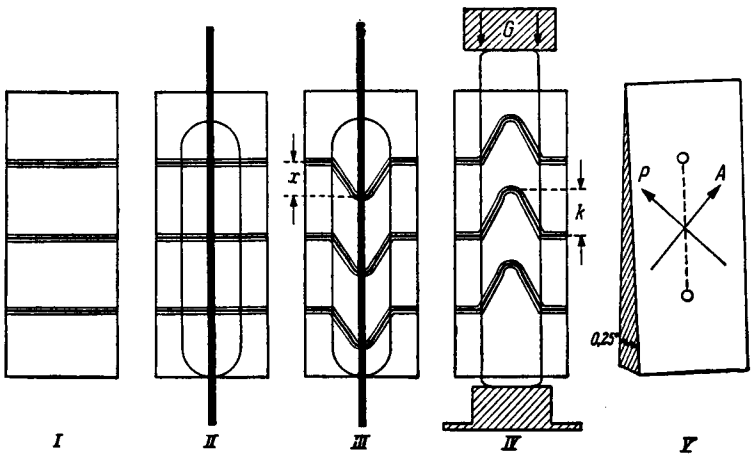


Fig. B 10-181 Fields of view obtained when measuring strains in glass with monochromatic light and quartz wedge, set-up as in Fig. B 10-182

I quartz wedge alone

II wedge with interposed strain-free glass rod in which a metal lead-through is coaxially sealed

III as II, but glass rod strained by expansion mismatch with metal. The size of x is a measure of longitudinal stress

IV calibration of shift (proportional to stress) by loading with a known weight G (kg) an equal rod of glass without internal stresses and with the same composition. Shift k thus corresponds to a stress $\sigma = G/Q$, where Q is the cross-sectional area of the glass rod. The significance of the direction of shift: in the example shown upward shift means compression, and in III the downward shift means tension (axial)

V position of the quartz wedge in the field of view: ○ – – – ○ is optical axis; P and A are axes of vibration of light that passes through polarizer and analyzer

out of the visible spectrum and the complementary red-violet shows up. In this way, one can set up a complete color scale for each path or phase difference, but which only shows marked differences in color for relatively large path differences, of little interest in the case of glasses (see Table T 10–23, cols. 1 and 2).

A considerable improvement in detectability of small strains is brought about if, instead of measuring the values of Δ (the path difference caused by strains in the test-piece) from zero, a delay disk (called "sensitive tint plate") is inserted between the crossed polarizers which introduces a fixed path difference Δ_0 = 565 mμ, i.e. removes the yellow-green spectral colors and substitutes a red-violet background. The values of Δ produced by strains in the glass are then added or subtracted to or from Δ_0. For

example, a gypsum or mica plate of suitable thickness can be inserted, whose optical axis must lie at 45° to the polarization planes of the polarizer and analyzer. Since such a mica plate colors the background a red-violet, it is described shortly as "mica plate

[10.3]

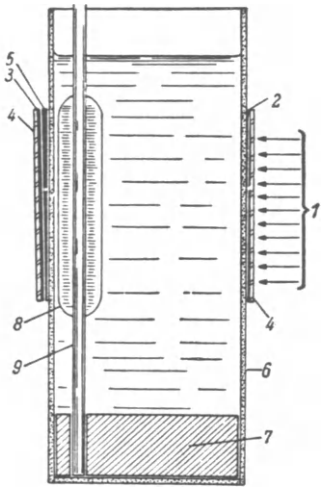
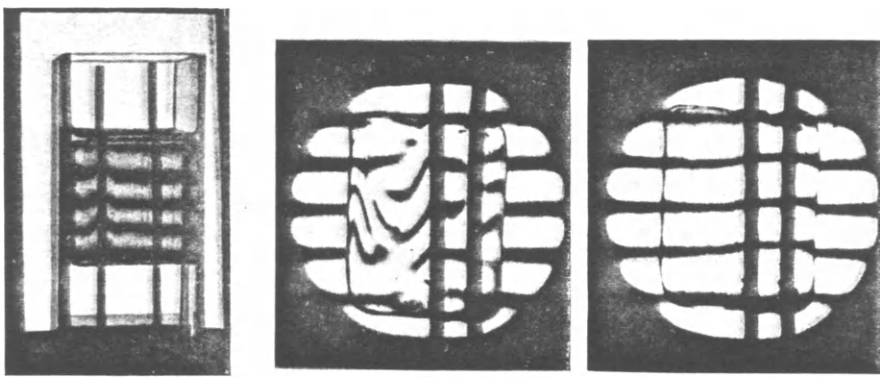


Fig. B 10-182 Arrangement for measurement of strains in glass with a quartz wedge ([3]HULL)

1 incident monochromatic light-ray (from filament lamp, filtered by green Wratten filter N 62); *2* first polaroid film (polarizer) with protective glass; *3* second polaroid film (analyzer); *4* protective glass; *5* quartz crystal wedge, cemented to analyzer and protective glass; *6* glass tank with benzene and alcohol or CS_2); *7* holder; *8* cylindrical glass test-rod; *9* metal rod sealed coaxially in glass

of red-violet I order". Besides this plate, ones for $\Delta_0 = 530$ mμ ("red I order") and $\Delta_0 = 575$ mμ ("violet I order") are sold. Knowledge of the Δ_0 values of the delay disks or plates used is obviously important for precise color evaluation from tables of colors (e.g. Table T 10–23, cols. 3–5).



I II

Fig. B 10-182 A Photographs of stress patterns in a glass-metal seal taken with the aid of a quartz wedge

I apparatus of type in Fig. B 10-182 with two different symmetrical glass–metal seals made of rods; *left:* tensile stresses[1] of about 0.5 kg/mm² due to mismatch in expansion coefficients of glass and metal; *right:* well-matched, strain-free seal ([3]HULL)

II twin Mo-wire seal in glass; *left:* strained by cooling from 850° in free air; *right:* the same seal after tempering in furnace ([2]DOUGLAS)

[1] Since in the figure the thick end of the wedge is up, the shift of the dark lines upwards indicates tensile stresses (axial)

In the case described above, strains in the glass produce a path difference which in turn produces a change in the red-violet background color either towards a blue or an orange tint, corresponding to addition and subtraction from Δ_0 respectively. These changes are given in Table T 10–23, cols. 3–5, for various magnitudes of Δ. As can be seen, relatively small path differences can be easily detected by large changes in color,

TABLE T 10–23. COLORATION OF STRAINED GLASS VIEWED IN A POLARISCOPE WITH A "WHITE" LIGHT SOURCE[1]

[10.3]

WITHOUT DELAY DISK (SENSITIVE TINT PLATE)		WITH DELAY DISK 565 mμ [2]		
1	2	3	4	5
PATH DIFFERENCE Δ[3] (mμ)	COLOR	PATH DIFFERENCE Δ[3] (mμ)	"BLUE" DIRECTION	"ORANGE" DIRECTION
50	Iron grey	0	Violet	Red-violet
200	White-grey	23	Blue-violet	Red-violet
300	Yellow	46	Blue	Orange-red
425	Orange	69	Greenish blue	Orange
530	Red	92	Bluish green	Yellowish orange
565	Red-violet, purple	115	Yellowish green	Gold yellow
640	Blue	150	Dark green	Gold yellow
675	Bluish green	180	Green	Yellow
740	Green	220	Bright green	Bright yellow
840	Yellow green	290	Greenish yellow	White
880	Yellow	330	Bright yellow	White
> 880	[4]			

[1] Axes of polarization of polarizer and analyzer mutually normal. Optical axis of test-piece bisects the right angle between axis of polarizer and of analyzer.

[2] Optical axis at 45° to axis of polarization of polarizer.

[3] Due to strains in the test-piece.

[4] As the path difference increases, the colors repeat themselves in the same serial order but with some slight difference in tint; colors of "higher order" appear. In technical glasses, however, the colors produced by path or phase difference are mostly of the first order.

as the eye is specially sensitive in the λ range around 565 mμ. If the background color of the field of view is not altered, or is partly unaltered by the glass test-piece, then there is no strain at the area concerned only if no change of color occurs for *all* directions of the test-ray, as shown by oscillating the test-piece about its normal position. This is because strains or stresses whose directions lie wholly in the line of sight of the observer, or are parallel to the plane of polarization of a polarizer, produce, as stated, no optical effect and would therefore be mistaken for absence of stress.

Since the tensile strength of glass is only one tenth of its compressive strength, it is important to know whether the color change to blue or to orange is based on a compressive or tensile stress. The answer is found most simply by bringing a straight, strain-free glass rod into the field of view and setting it at 45° to the plane of polarization of the analyzer; its axis is then slightly bent so that on the concave side of the bend there will be longitudinal compression and on the convex, tension. One can now directly

determine which color change in the apparatus corresponds to which type of stress. For the same purpose, a soft glass rod with a W rod sealed in the center can be used. The relatively low thermal expansion of W produces substantial tensile stress along the axis of the glass rod, and this will indicate as before which color change goes with tension, the kind of stress which most has to be watched. If, as in the color photographs of Fig. B 10-182C, the axial tensile stress is parallel to the optical axis of the interposed delay plate, path difference Δ is subtracted from the permanent value Δ_0, i.e. there is a color change in the orange direction; under the same conditions but with compression, there is addition, i.e. color change in the blue direction. Obviously, if the stress vector lies at 90° to the optical axis of the delay plate, the stated color changes are reversed in direction. The illustrations in Fig. B 10-182B are color patterns from glass test-pieces as they appear in a strain-viewer with a white light source and a delay disk type "red" (in this case a gypsum plate); the color photos in Fig. B 10-182C are systematic measurements on a specially shaped glass–metal seal for testing sealing alloys.

[10.3]

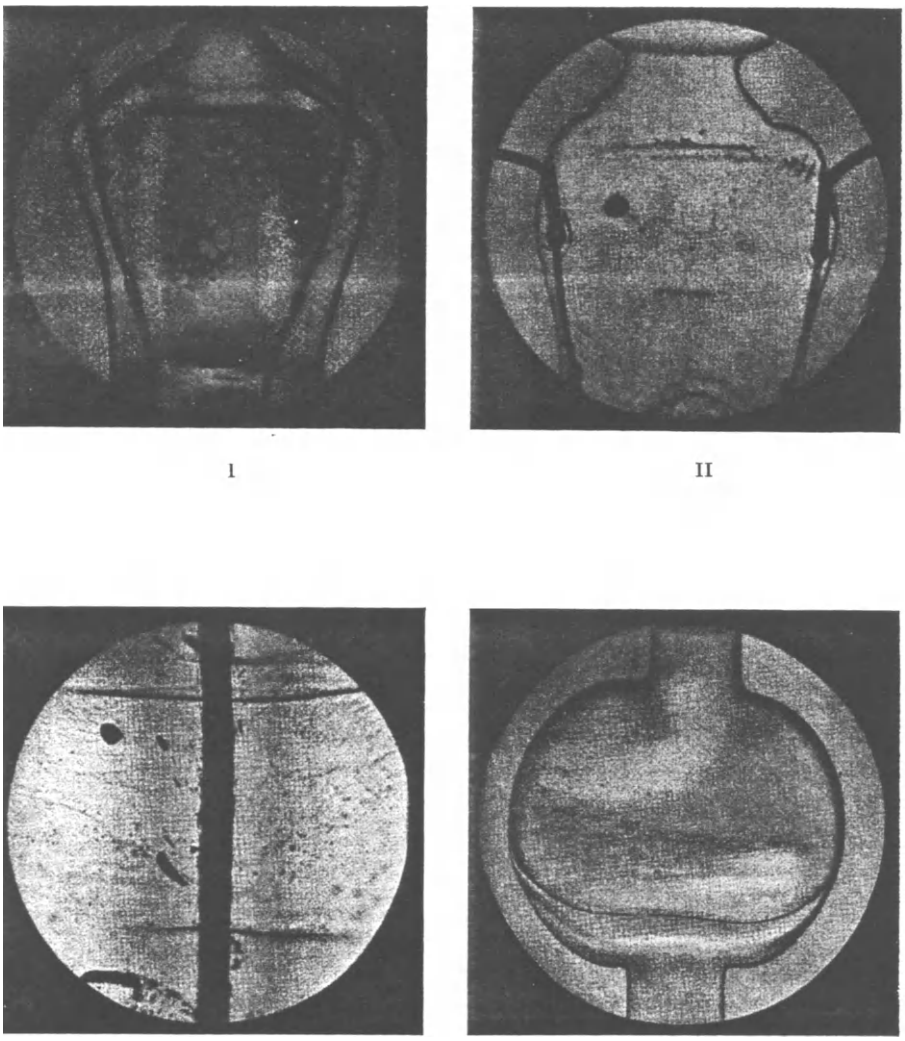
When testing for strains with the aid of Table T 10–23 it should be noted that if the glass has an irregular shape, the path difference, and with this the colors, do not only vary with the spatial variations in stress but with the thickness of glass traversed by the test-ray of light. Glasswork of similar shape and with the same stresses can therefore show different interference colors if their thicknesses differ, a point to be watched in mass-production. For quantitative results on stresses in a glass object, the path difference per cm, Δ/d (mμ/cm) should always be determined. The same applies to measurements on stressed test-pieces of the same shape but different types of glass because of the variation in photoelastic constant. Comparative tests using a reference specimen annealed in a prescribed way—a method often employed on mass-production—is also only permissible if the master has the same shape and dimensions, is the same type of glass, and is examined from the same angle as the products under test.

Most of the established strain-viewers with white light sources used in practice are constructed along the lines described and only differ in the methods of construction of their components.

The simplest strain-viewer is the so-called "polarization glasses". In this method, daylight from a window falls at an angle of 50–60° to the vertical on to a reflecting dark (not white or metallic) surface such as a black glass or celluloid plate, or if the object tested is very large, as in Fig. B 10-183, on a highly polished linoleum or parquet floor with a mirror finish. The test-piece of glass is then observed, preferably at 30–40° to the horizontal, by reflected light polarized linearly by the polarizing glasses. These glasses consist of a polaroid film (see below) as analyzer and a red I filter. The specimen is turned slowly back and forth on the line of sight as axis, and the strained areas appear alternately blue and yellow, while unstrained areas remain red to red-blue like the background. Clarity and brightness of the effects are increased if a suitable dark visor or dark paint on the room walls ensures that both the test-piece and the eye of the observer receive polarized reflected light only.

Polaroids are generally large-area, thin plastic films in which small crystals of herapathite are embedded and lie parallel; the films are then cemented between two strain-free glass disks and mounted in circular frames under zero stress. Herapathite, a periodide of quinine sulfate is a dichromatic crystalline substance which, like tourmaline,

[10.3]



I II

III IV

Fig. B 10-182 B Color photographs of various glass test-pieces in a strain-viewer, with the aid of a gypsum plate, of order "red I" ([2]SPÄTE)

I highly stressed filament lamp pinch-foot; II annealed pinch; III strains produced by unequal match of expansion coefficients of Pb-glass and sealed-in Cu wire; IV strains due to mismatch between two glasses joined together by melting

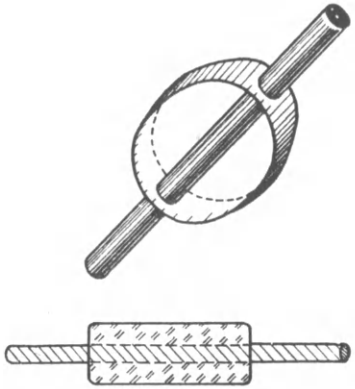
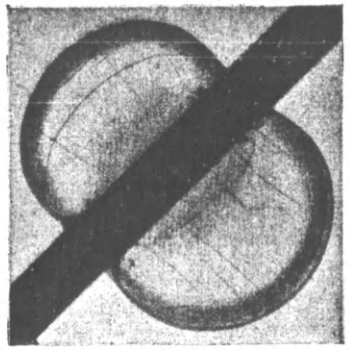


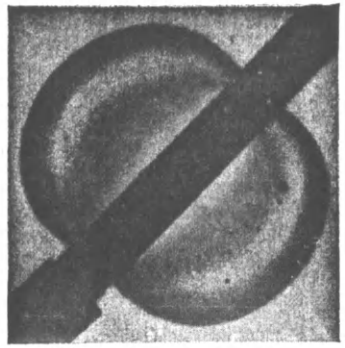
Fig. B 10-182c I

Z 1



Z 2

Z 3



Z 4

Z 5

Z 6

Fig. B 10-182c II

Fig. B 10-182c III

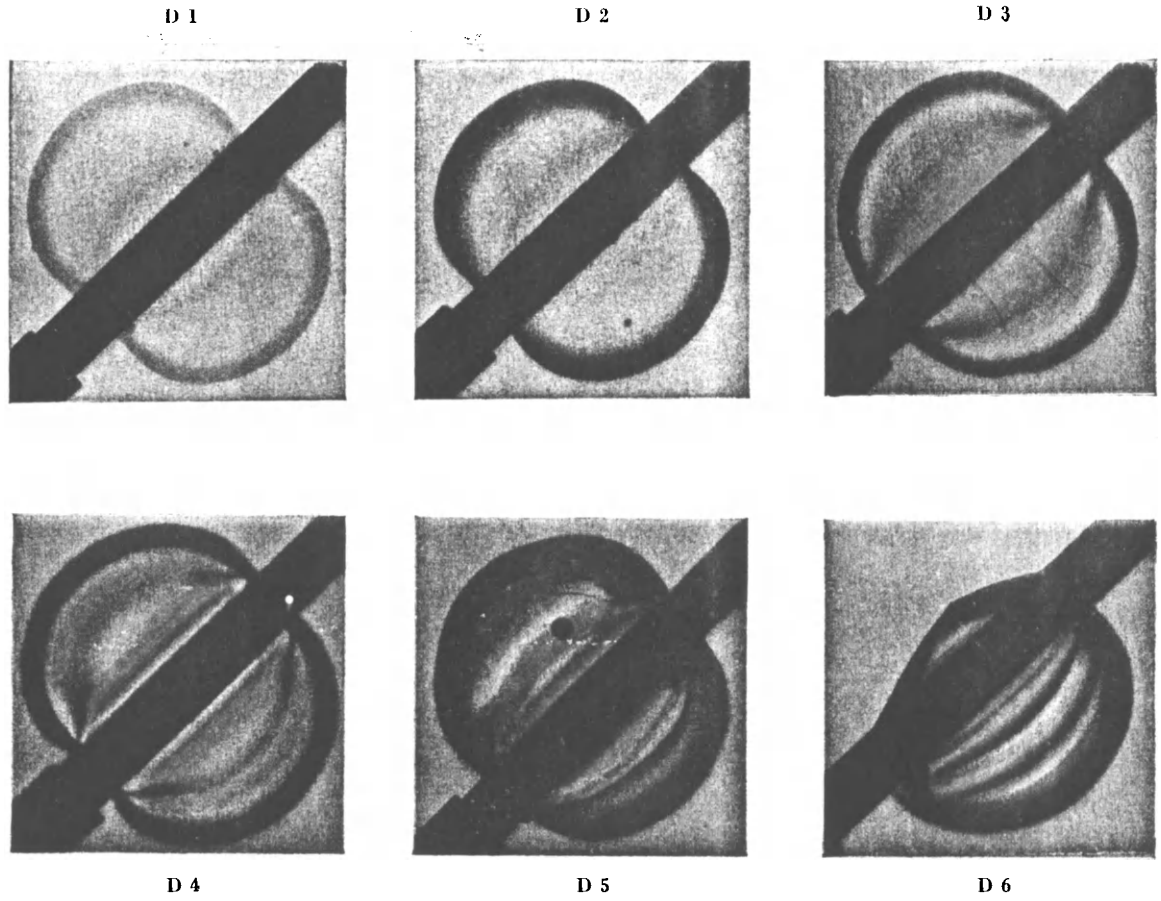
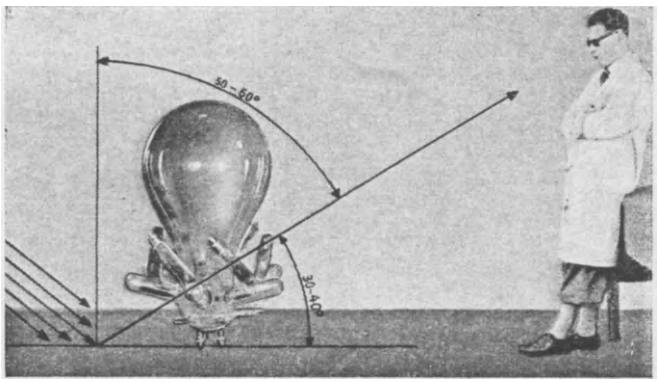


Fig. B 10-182c Stress patterns (in color) that appear in a polariscope examination of a glass test-piece sealed to metal. A gypsum plate ("red I order") was used, and the photographs come from [2]HERRMANN

I shape of test-piece; II color pattern seen when object is strain-free; III Z_1 to Z_6 are patterns corresponding to stepwise increase in tension along the seal-wire axis; the path differences produced by the gypsum plate is reduced by the birefringent test-piece, the red background turns orange to yellow and in Z_4 to Z_6 the tension stresses are as shown, since the glass cracks at this load; IV D_1 to D_6 correspond to stepwise-increasing axial compressive stress and the basic path difference is increased, the color changes to dark blue, then bright blue and finally to green and yellow until it reverts to red I (D_4); at D_5 and D_6 fracture of the g ass again relaxes the stresses

Fig. B 10-182c IV

absorbs one of the polarized beams produced by birefringence so strongly that it is almost opaque to it. A single bare film of this material without a glass cover transmits about 34% of normally incident white daylight as linearly polarized rays, and only 0.6% as ordinary visible light. Such polariod filters can be used without difficulty up to 30° entrance angle (aperture). These filters are supplied by firms such as the SHEET POLARIZER CO. INC., Union City N.J., USA, and recently VEB CARL ZEISS, Jena,
[10.3] GDR. Cf. also HAASE, RÖSCH.



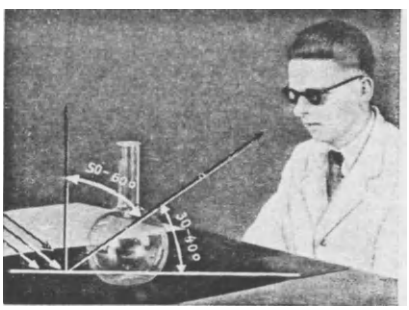


Fig. B 10-183 Strain-testing a large glass envelope with a pair of ZEISS polarization glasses, consisting of polarization and red I filters (BARTELS)

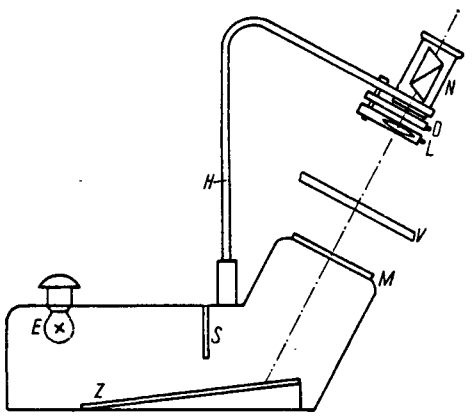
Floor or table-top cover of smooth red-brown linoleum polished to a mirror-finish, to produce reflected and polarized light

Figure B 10-184 shows the general design of a polariscope well-established in electron-tube production, and the commercial model can be seen in Fig. B 10-185: the polarizer Z consists of a black reflecting glass disk illuminated by a filament lamp set at the best angle for polarization, and the analyzer N is a NICOL prism whose polarization plane is normal to that of the test-ray. A rotatable and interchangeable red-violet I filter (gypsum plate) permits strain measurements in the red-violet field of view with a fixed path difference of 582 mμ; a retractable magnifying glass enables specially interesting details of the stress pattern to be seen.

The polarization angle φ referred to above for light incident on glass lies between 56° and 63° to the vertical for refractive indices $n = 1.47$ to 1.92, where $n = \tan\varphi$, a well-known relationship. The degree of polarization is 100% at this angle, and at small deviations the reflected light is still predominantly polarized. The linearly polarized light

yield as a percentage of the incident light intensity is small, however, and for a black glass mirror of $n = 1.53$ amounts to 8% only, and is about 13% for $n = 1.75$.

The polarizer of the equipment in Fig. B 10-184 (NICOL, or similarly made GLAN-THOMPSON prism) consists of two calspar prisms cemented together with opposed wedge angles. Both are birefringent and of the two rays so produced, the ordinary ray is



[10.3]

Fig. B 10-184 Construction of a strain polariscope for quality control of stresses in glass (see Fig. B 10-185 for actual model)

E filament-lamp source; *S* screen to mask-off light; *Z* black glass mirror (polarizer); *M* ground-glass screen; *V* glass test-piece; *L* retractable magnifying glass for resolving fine details in stress pattern; *D* rotatable and interchangeable delay disk (gypsum plate "red I order"); *N* Nicol prism analyzer; *H* support bracket

Fig. B 10-185 Model of a commercial strain-viewer for glass (see Fig. B 10-184), with 170 mm dia. field for test-pieces up to 600 mm dia. (Type GSP 1, made by R. PLAGWITZ, OPT. PRÄZ.-ANSTALT, Berlin-Lankwitz)

totally internally reflected at the cemented interface and absorbed at the blackened side surface, so that the second, also polarized extraordinary ray is transmitted. The main advantage of the Nicol over the polaroid filter is its 100% polarization, and its main disadvantage is that the aperture and field of view lie within narrow limits.

Figure B 10-186 shows a simple polariscope (non-adjustable) with crossed polaroids and red I filter, originally developed by CARL ZEISS, Jena, for strain-viewing spectacle lenses but suited for testing small mass-produced components like horizontal press-feet

[10.3]

Fig. B 10-186 Polariscope for one-off testing of small glass components, made by ZEISS, Jena

Polarizer and analyzer are crossed polaroid filters. The delay disk of "red I order" is fitted in the ocular

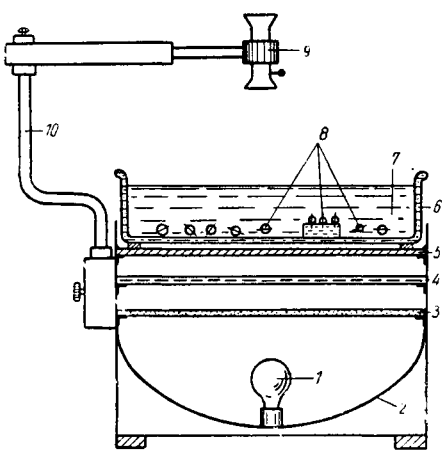


Fig. B 10-186A Polariscope for quantity testing of small glass-insulated lead-throughs (construction see Fig. B 10-186)

1 light source (filament lamp); *2* reflector; *3* ground-glass screen; *4* polarizer, polaroid film between two glass protection disks; *5* cover of mirror glass; *6* immersion tank of annealed glass; *7* immersion fluid; *8* test-pieces; *9* rotatable analyzer with mica plates, "red-violet II order"; *10* 2-way adjustable holder

without exhaust stems (Fig. B 10-134). Figure B 10-186A shows the principle of a device made with similar components for use on small mass-production parts. Figure B 10-187 shows English-made apparatus very like that in Fig. B 10-186 for testing press-feet in an electron-tube factory. An American unit is illustrated in Fig. B 10-188;

polarizer and analyzer are made of especially large polaroid filters. It was developed by EISLER for direct-vision testing of, primarily, large TV tubes. These are available commercially in four sizes with 3, 6, 9, and 12 in. dia. field of view. Recently these large-area strain-viewers have become available in Europe as portable models. (See Fig. B 10-188A.)

[10.3]

Fig. B 10-187 Polariscope testing of press-feet for strains (courtesy of GEC-OSRAM, Wembley, England)

Projection polariscopes, using the polaroid filters described, have also been developed; the interference pattern of the strained test-piece (max. field of view 25×25 mm) are projected onto a ground-glass screen. Figure B 10-189 shows the diagram of this equipment whose overall dimensions are $600 \times 500 \times 450$ mm, and which is provided with a red I filter, an immersion tank, a large projection lens and a mirror system, so that the image (magnified $\times 12$) appears erect and not reversed on the ground-glass screen which is let into a recess on the front panel.

For approximate quantitative determination of strains in glass by means of these polariscopes when operating with white light, a stepped wedge (Fig. B 10-190) gives sufficient accuracy for works use. It is made from mica sheets with parallel polarization

[10.3]

Fig. B 10-188 Strain-viewer with polarizer and analyzer of large polaroid films for direct viewing. Field of vision up to 300 mm dia. (made by EISLER ENG. Co., Newark, N.J., USA)

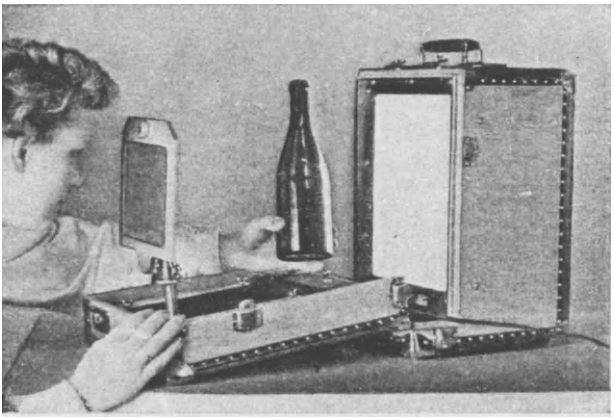
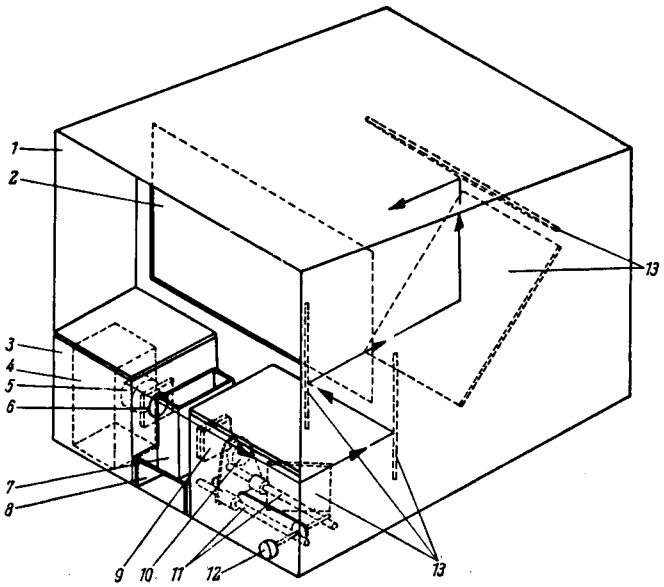


Fig. B 10-188A Portable large-area strain-viewer (9 kg); polarizer 300×200 mm, analyzer 110 mm dia. (made by Dr HEINRICH SCHNEIDER, Optotechnische Fabrik, Bad Kreuznach; larger versions can be supplied)

planes, and their thicknesses are so graded that they produce on a "violet I order" background in the polariscope a scale of colors corresponding to 30 mμ path or phase difference each step. The stepped wedge and the test-piece are arranged in the measuring



[10.3]

Fig. B 10-189 Design of a projection polariscope (from FORTEY)

1 metal frame; *2* ground-glass screen; *3* lamp housing; *4* projector lamp (250 W); *5* duplex condenser lens; *6* polarizer (polaroid filter); *7* immersion tank for test-piece; *8* pedestal for *7*; *9* "red I filter" and analyzer (polaroid disk); *10* projection lens (150 mm dia., *f* 3.5); *11* slide for lens; *12* focus control for projection lens; *13* glass front-surface mirrors, Al evaporated coating (five off)

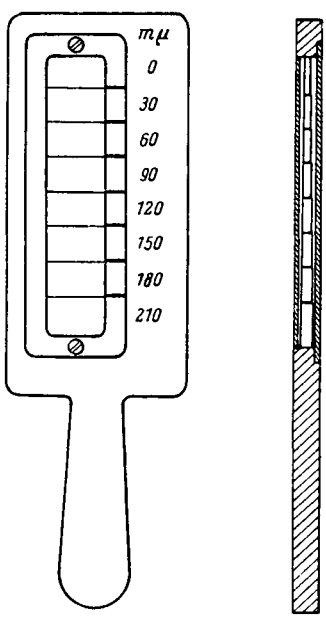


Fig. B 10-190 Stepped wedge of mica, for quantitative determination of stresses in glass ([2]KRATOCHVÍL)

field of an ordinary polariscope so that the wedge is parallel to the test-direction of the test-piece; then a scale of path-difference values are read off for that step of the wedge whose color best matches that of the observed part of the test-piece. These values ($m\mu$) are then divided by the glass thickness or, more correctly, by the path length (cm) of the polarized light ray in the test-zone of the glass body.

The polarization microscope (Fig. B 10-191) provides exact quantitative determination of the stress trajectories in a glass body by point-to-point measurement of stress. Details of operations with this device are given by RINNE, A. F. ROGERS, GAUSE, and

[10.3]

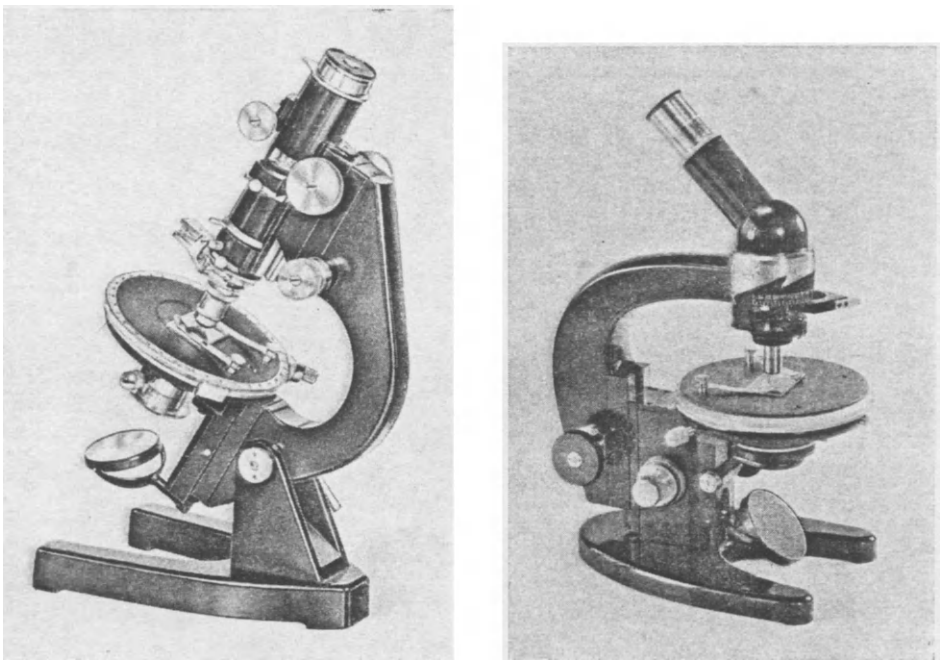


Fig. B 10-191 Polarization microscopes
I type CM, with polarizing prism or filter (made by E. LEITZ, Wetzlar)
II type LgOB, with polarization facility (made by VEB Carl ZEISS, Jena)

PILLER, for example. HERRMANN describes a simple set-up for measurement of stress at high temperatures using the microscope, suitable for examination of glass–metal seals. The instrument is in principle a standard microscope, generally of low magnification; below the condenser it is fitted with a polarizer (Nicol or polaroid filter) and in the tube between objective and ocular there is an analyzer (again a Nicol or polaroid filter) and also a so-called "compensator". A compensator is a transparent sheet of birefringent crystalline material whose thickness as traversed by the test-ray of light, and therefore the phase or path difference it produces, can be varied continuously and measured by a micrometer screw. (There are different types: the BABINET type contains a quartz crystal wedge combination; the BEREK (Fig. B 10-193) is a calspar plate, 0.1 mm thick, set obliquely in the light-beam by micrometer adjustment, and the variable path differ-

ence is read on the scale divisions of the micrometer screw. The first type will enable path differences to be read to ± 5 mμ, and the second type to ± 2.) (See HOLLAND, READ, for further details on compensators and their use in strain measurements on glass.) Monochromatic light is usually employed, e.g. a Na-vapor lamp ($\lambda = 589.3$ mμ) or a filtered Hg-vapor lamp ($\lambda = 546.1$ mμ) and without sensitive tint delay plates. When a BABINET compensator is used (Fig. B 10-180, right), the field of view consists of a series of parallel dark lines or bands at positions where the path difference produced by the compensator is $0\,\lambda$, $1\,\lambda$, $2\,\lambda$, etc., where λ is the wavelength of the monochromatic light employed. If now a stress-free test-piece is placed on the stage, the field of view is virtually unaltered (Fig. B 10-192, I). Strain in the test-piece will lead to path differences (Figs. B 10-181 and B 10-182A) and thus to shift of the dark lines in the field, the size of the shift being proportional to the stresses at various points in the test-piece. Examples are given in Fig. B 10-192, II, III. By turning the micrometer adjustment for the compensator, one can make the lines shift back again and so read off the path or phase difference on the scale of the compensator adjustment, as equal to the number of scale divisions needed to reset the lines at each position observed. The observed field of view is somewhat different if a BEREK compensator is used (Fig. B 10-193). Here, the path difference produced by the glass under test is compensated (by turning the micrometer screw) until the ocular shows a dark field exactly at the point under examination, which

[10.3]

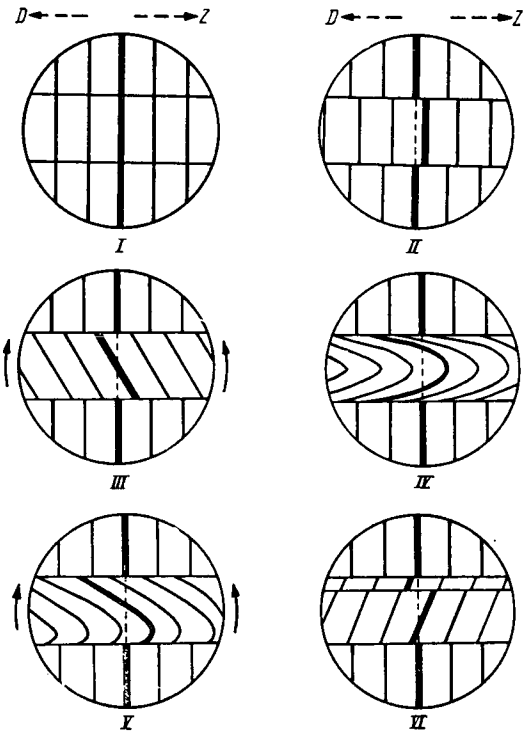


Fig. B 10-192 Stress patterns (from HOLLAND) in the field of view of a polarization microscope using a BABINET compensator (quartz wedge). D = compression stress vector, Z = tensile stress vector

I lines in unstressed glass; II *idem* under constant tension; III *idem* for simple bending, concave upwards, compression above, tension beneath, neutral zone in center; IV pattern of rapidly chilled glass (outer axial compression, internal tension with maximum in center of rod); V as IV, bent concave upwards: upper compression is increased, the previous compression below is converted to tension and the zone of max. tension shifts from the center downwards; VI stresses in glass sheathed on one side with another glass, produced by unequal expansion coefficients of the two glasses

is at the intersection of cross-wires provided in the compensator. (See HOLLAND, RINNE, for further details.)

The use of a compensator also permits quantitative measurements of stress or strain in $m\mu$, especially at areas of peak stress, or a whole stress pattern can be found by a number of measurements at various points of the glass test-piece as it is turned and moved on the stage of the microscope. Accuracy is much increased by grinding plane

[10.3]

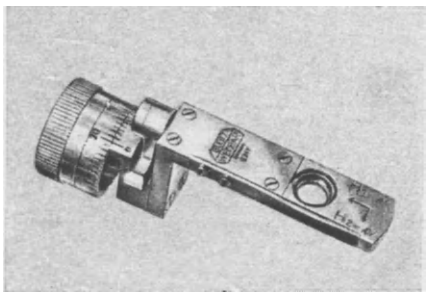


Fig. B 10-193 BEREK compensator for quantitative determination of stresses in glass using a polarization microscope (made by E. LEITZ, Wetzlar)

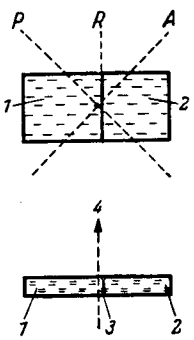


Fig. B 10-193A Control testing of deviations of the expansion coefficient of a glass by comparison with a standard specimen, using a polarization microscope to measure strain (from PADMOS)

Above: view of the joined disks in the microscope: *P* direction of polarization in polarizer; *A* as *P*, for analyzer; *R* line of joint between disks, 45° to *P* and *A* = direction of stress in joint = optical axis of compensator; test-ray is normal to the paper, measuring zone is round intersection of *P* and *A*.

Below: *1* cross-section of standard glass disk, 10×10×3 mm; *2* the same for the test-piece; *3* smooth-ground, then fused surfaces of both disks; *4* test light-ray path

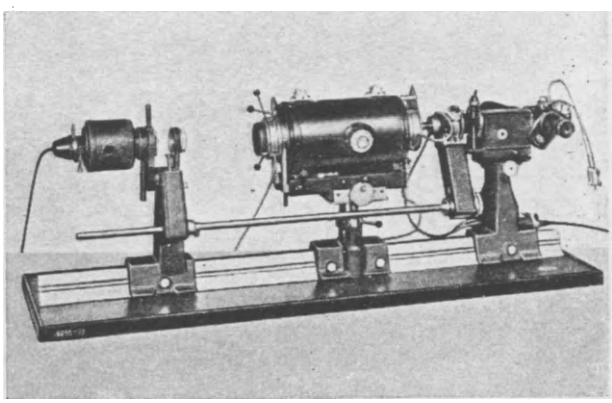


Fig. B 10-193B Large commercial "hot-stage" polarization microscope (maker and supplier of photograph: E. LEITZ, Wetzlar)

parallel flats back and front of the zone of the glass that it is desired to examine under the polariscope. This will not only avoid harmful reflexions, especially total reflexion, but it enables the glass thickness to be found more precisely.

Unfortunately, as can be seen, measurements with the polarizing microscope are rather time-consuming, and it is therefore mainly employed on development work in the laboratory. However, in simplified form, it can serve as a reliable instrument for control of constancy in glass manufacture. Figure B 10-193A shows an instructive example of this (PADMOS) taken from the manufacture of technical glasses by PHILIPS, Eindhoven. Square plates $10 \times 10 \times 3$ mm are made from the test glass (spot-checks from a day's production) and a standard glass. Both equal-sized plates are ground flat on an edge (10×3 side) and fused together along these edges to make a single plate $20 \times 10 \times 3$ mm, in an ordinary glass-working torch. The interface is only fluid for a short time so that the changeover zone between the two plates is clearly visible. Directly after sealing, the plate, still hot, is put in a tempering furnace, annealed and slowly cooled (Fig. B 10-169 and Table T 10–21). Now the only stress in the plate is that produced by any differences there may be in expansion coefficient between the two glasses, and this effect would be a maximum at the fused joint. Such stress can be quantitatively determined, by the polarization microscope and compensator, in the standard plate and in the direct neighborhood of the joint line, if the test-ray is normally incident on the plate and the joint line makes an angle of 45° with each plane of polarization of the polarizers (Fig. B 10-193A, top). The path difference thus obtained, together with establishment of the stress direction, is a far more precise measure of deviation from nominal values of the expansion coefficient of any glass products than is the much more complex direct measurement of expansion characteristics in a differential dilatometer; precision of the polarization method corresponds to a difference in α of only about 0.15×10^{-7} l/°C. Besides, a fairly careful dilatometer measurement requires at least 8 hours, and the PHILIPS process easily tests 15–20 per day, employing one person who needs no special training. [10.3]

See Figs. B 10-11 and B 10-12A for polarization measurements of strain in glass at elevated temperature, and especially for following isothermal annealing processes over periods of time.

In the manufacture of glass–metal seals it is useful to know quantitatively how the stress trajectories in glass at the seal zone vary with time and position over the whole course of annealing and renewed heating (occasioned by practical use) ([1]ENGEL). In this case a polarization microscope which will measure stress in heated glass–metal seal test-pieces is needed. Such "polarization-furnace microscopes" have recently been marketed by E. LEITZ, Wetzlar; cf. Fig. B 10-193B.

10.4. Surface Treatment of Glass

10.4.I. *Mechanical and Chemical Cleaning*

(LAUG, MINDT, WOYTACEK)

Cleaning is usually necessary in the manufacture of sealed-off HV or gas-filled tubes, partly to prevent gassing from dirty surfaces during subsequent operation of the tube, and partly to achieve the best possible adherence of applied coatings (e.g. metal mirrors) or to prevent killing of fluorescent layers. Degassing of clean, i.e. contaminant-free, surfaces is treated in 10.5. [10.4]

(a) *Mechanical cleaning*, especially with hard tools (steel wire for capillaries, hard wire-brushes) should be avoided where possible, since even slightly scratched glass tends to crack along the axis of the tubing. Only in special cases is washing off with a soft brush, or mechanical abrasion by glass balls (see section (i)), permitted. In the normal way, dirt, grease or dust is removed by wet methods, i.e. by washing in chemical reagents and water. There is a whole series of recipes in common use, varying with the special requirements of each case, and the most important are given below.

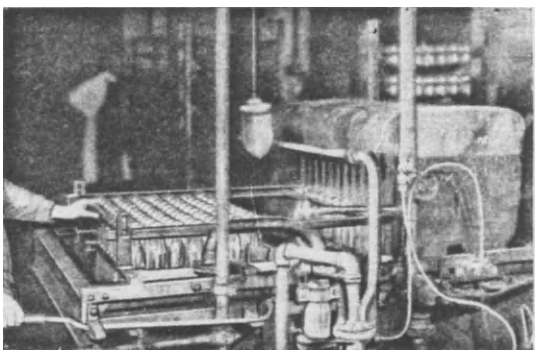


Fig. B 10-194 Machine washing of glass envelopes before further working (courtesy of TELEFUNKEN-OSRAM)

(b) *Cleaning raw glass stock:* bulbs and tubing when supplied from the works in not too dirty a state are usually cleaned before further working into lamps or tubes by stacking in racks in large containers lined with Pb sheet (Fig. B 10-194), where they are sprayed inside and out with 1–5% HCl for 3–5 sec. They are next sprayed with hot (40–50°) water at about 1.5 atm pressure, and finally the residual H_2O is blown off by oil-free compressed air (*ca.* 300 mm Hg gauge) for 1–2 sec. Often a rinsing in distilled water is given before blowing off, to avoid water marks. Recently, increasing use has been made of demineralized (deionized) water (BAYFORD) instead of distilled water, for cheapness. This water is obtained from "ion exchange columns" (see, e.g., ŠMÍD), and piped through polythene tubing to the individual working areas, its purity being controlled continuously by conductivity measurements. An idea of how much pure water can be used in washing large tubes is seen from the following example: for an output of 50,000 TV tubes per month, three demineralizers of 5 m^3/hr throughput are needed (HÜHN), i.e. 10,700 m^3/month or *ca.* 200 liters/tube. Taking into account rejects, reserves and possible delays, about 100 liters pure water is needed for every picture tube that goes into production.

The final drying of washed envelopes takes place generally in pre-warmed dust-free air. If envelopes are not due to be worked immediately, they should be stored in a dust-free atmosphere and before sealing should be quickly washed again with hot KOH solution (see below), hot pressurized water and deionized water.

(c) *Cleaning magnesia-glass envelopes*: immersion in a 3–5% acetic acid solution which can be used for a large number. Wash off all acid in tap water, then in deionized water. Place on filter paper for water to run off. Dip in alcohol. Allow to drain off, then remove residual alcohol by centrifuging. Possibly remove stains with chamois leather. [10.4]

(d) *Degreasing glass* (especially ground-glass joints): wash in acetone. Wash in 10% heated sodium carbonate, or in an aqueous solution of potassium bichromate ($K_2Cr_2O_7$). Rinse in hot distilled water, then methanol. Dry with anhydrous dust-free air.

(e) *Cleaning glass surfaces before applying front-surface mirrors* (from YARWOOD). Detergent wash. Rinse in tap water. Dip in concentrated chromic acid until water wets the glass evenly. Warning: strong soda solutions etch the surface.

(f) *Cleaning photocell envelopes before mirror coating*: wash inside with sodium bichromate + HCl solution, which can be made as follows: 100 g $Na_2Cr_2O_7$ are dissolved in 600 ml distilled water in an ERLENMEYER flask over a water bath at 60°. 300 ml HCl are slowly added, taking care because of the heat of reaction. Store in well-sealed glass flask. Rinse as in (g).

(g) *Cleaning heavily-contaminated glass*: pre-wash in strong KOH or NaOH, rinse in tap water. Wash off in concentrated chromic sulfuric acid (see below) for a few minutes or a few days, according to degree of contamination. Rinse in pure water, with caution because there is strong heat of reaction with residual acid. Rinse in distilled water, preferably boiling in several changes thereof (LAUG). Small parts are then rinsed in pure ethanol. Hot-air dry.

Oxide-contaminated glass near Housekeeper seals of large transmitter tubes can also be cleaned by washing in chromic sulfuric acid, then rinsed in distilled water and hot-air dried.

Chromic sulfuric acid is made as follows: powdered $K_2Cr_2O_7$ is dissolved for several days in concentrated H_2SO_4. Only brown (not green) colored acid to be used. Note here that glassware for biological purposes must not be cleaned with washing agents containing Cr, since Cr is very hard to remove completely from glass. Glassware cleaned with such agents will have the Cr leached out by the contents of the vessel, and this kills the lower organisms ([4]WEYL).

(h) *Cleaning in 2% HF*, made by dissolving 5 ml of 40% As-free HF in 95 ml distilled. Cleaning time 1–5 minutes, which slightly etches the glass but does not frost it. Envelope then sprayed with water jet. Wash TV tubes in hot NaOH solution. Rinse off with hot pressurized water. Wash in distilled water at 40°, or in deionized water at same temperature (see Section (b)). Rinse in ethanol. Dry envelope with a stream of hot, dry, dust-and-oil-free air.

(i) *Cleaning reject screens off TV tubes*. Where only small numbers are involved, the envelopes with their screens downwards are filled to 5–10 mm with carefully-cleaned glass beads, 1.6–2 mm dia. and distilled water. By forceful movement in every direc-

[10.4]

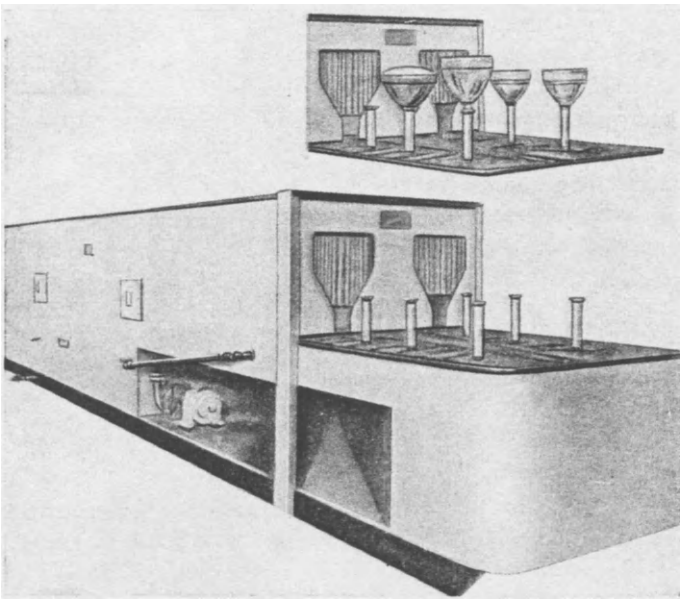


Fig. B 10-195 Glass envelope washing and cleaning machine. Used for TV tubes, especially those with reject screens or graphite coatings

Washing agents: ammonium difluoride or HF, hot NaOH and water. Tube-holders of Monel, spray chambers lined with Monel, conveyor belts of austenitic grey cast-iron (14–30% Ni, 4–7% Cu, 0.5–3.5% Cr and >1% Mo)[1]. Made by BETTER BUILT MACHINE CO., New York. Overall length *ca.* 9 m, height 1.8 m, width 1.4 m

[1] Trade name: "Ni-Resist 2", resists HF and hot NaOH; cf. *Metals Handbook* (1948), p. 518).

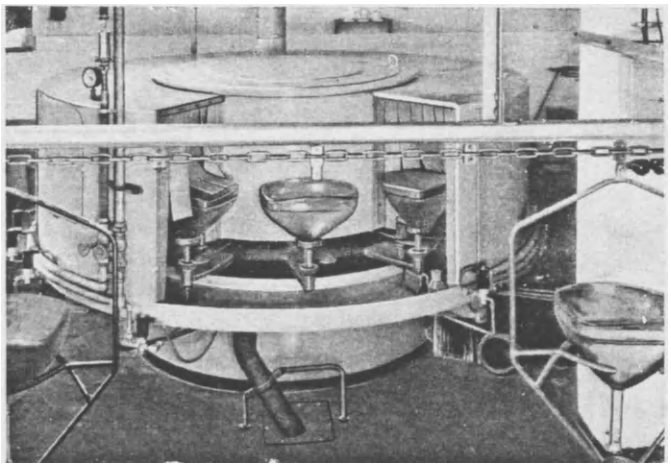


Fig. B 10-195A 12-position automatic turntable machine of 3 m dia. for washing large picture-tub envelopes (courtesy of TELEFUNKEN-RÖHRENFABRIK, Ulm)

The envelopes are sprayed in turn by a fine jet of 10% HF and then thoroughly rinsed several times with demineralized water, then finished with dry air

tion, the fluorescent coating is scoured off. The milky fluid is decanted and the beads tipped out. The surface is washed using a soft brush, rinsed in several changes of distilled water and finally hot-air dried. The glass beads are cleaned as follows: stir in chromic sulfuric acid for 10 minutes. Decant acid and wash off in suction-filter without filter paper. Rinse in distilled water. Allow to lie in rigid-PVC tank of 1% HF for 1 minute. Carefully wash in suction-filter with distilled water. Dry on glass dishes in drying cabinet. Store in wide-necked glass-stoppered flasks.

[10.4]

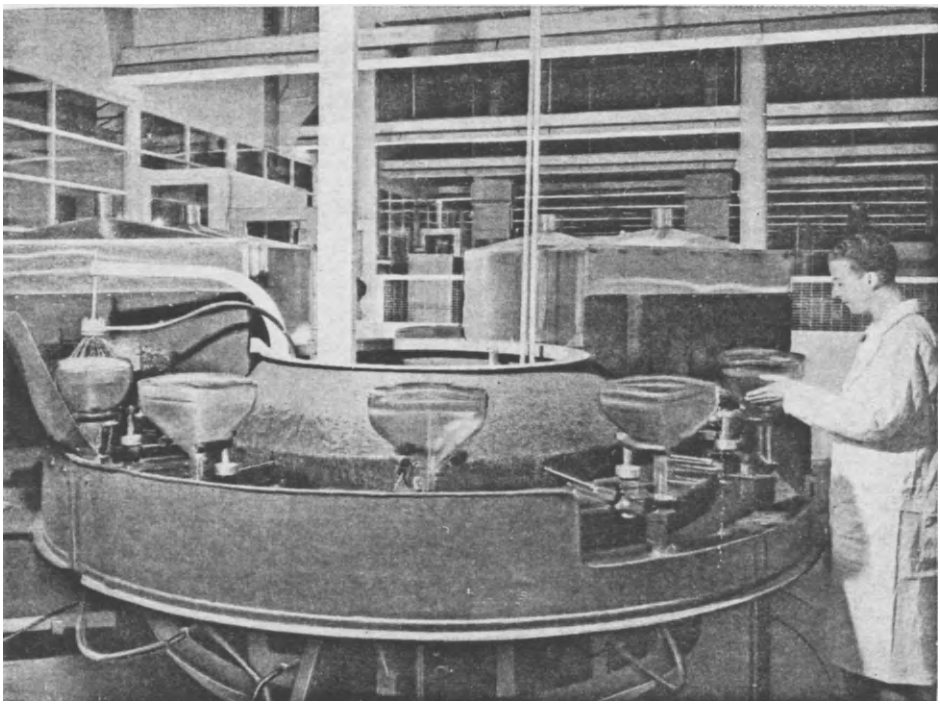


Fig. B 10-195 B Automatic rotary washing machine with 13 positions for internal and external cleaning of TV picture-tube envelopes. Reagents are NaOH at 45° and 7% HF, with intermediate rinses in tap water, and a final rinse in demineralized water (courtesy of FERRANTI LTD., Chadderton Works, Lancs., England; see also [19]ANON.)

On mass-production, cleaning is done in special automatic glass-washing machines of the type shown in Figs. B 10-195 and B 10-195A and B. The schedule is similar to that in (h) above; spraying serially with ammonium difluoride solution ($NH_4 \cdot HF_2$), or 2% HF — hot NaOH — tap water — distilled water, or spraying with 10% HF and thorough rinsing with hot water.

(k) *Washing very narrow-bore vessels.* Use apparatus described in Fig. B 9.4-4. After several rinsings with distilled water, it is recommended that the tubes be filled with, and laid in a vessel of, distilled water, and boiled for $^1/_2$ hour. The water in the tubes is then sucked out with the aid of the apparatus mentioned, and the tubes are finally dried at 110° in a drying oven.

(l) *Washing envelopes of HV diodes with oxide cathodes* to avoid the 10 V effect (see HAMAKER). The emission current of such tubes falls abruptly by more than 10% if 10 V plate voltage is exceeded. This effect is due to HCl vapor which escapes during the pumping process when the glass walls are heated to 400°, and is first taken up by the oxide of the cathode and then by the anode surface, and if the electron energy exceeds 10 eV, positive Cl ions are formed which can poison the cathode. The origin of this vapor is to be sought in the use of Na_2CO_3 as a constituent of the glass stock as this carbonate is contaminated with up to 1% NaCl. Besides use of Cl-free glass, lowering the degassing
[10.4] temperature from 400 to 200° and other measures (see HAMAKER), it is a help in such cases to wash the envelope with KOH solution before sealing to the electrode system to eliminate this troublesome effect.

10.4.II–VI. *Metalizing, Especially Coating Glass with Reflecting Surfaces*

(ANGERER, HEPBURN, METHFESSEL, PARTRIDGE, [1]STRONG, UMBLIA, WEHNELT, WEIN, YARWOOD)

Most of these processes are suitable for metalizing surfaces of quartz, ceramics, mica, and even plastics, or for coating a metal piece-part with another metal. Where special discussion does not appear necessary here, refer to the chapter dealing with the material concerned.

The inner or outer wall of a glass envelope must often be metalized. One reason is to produce high optical and thermal reflectivity as in the cases of Ag or Al mirrors inside or outside of spotlights or floodlights (Fig. B 10-161A), strip lights, IR lamps, or for Ag external mirrors on metal-vapor lamps to reduce cathode radiation loss, etc. Another reason is production of conducting surface layers, used directly as an electrode (e.g. internal metal coats for photocells to serve as substrate for the photocathode and for Geiger counter cathodes), or for leakage of surface charge and electrostatic screening of gas-discharge spaces. Finally, the process can be used for soldering metal parts to glass. Thin metal layers can be applied to glass by sintering (10.4.II), cathode sputtering (10.4.IV), or vacuum evaporation (10.4.V). Even when only a few Å thick, they can be soldered with In to metal connexions to make a relatively strong and low-resistance contact (see BELSER and 7.5, especially Table T 7.5–4). Such joints have shear strengths of 0.4–0.7 kg/mm². Fired-on Pt layers can be pre-tinned with pure Sn and then soldered to a Ag film using a Sn solder with 2–4% Ag, if care is taken; the 2–4% Ag is to prevent solution of the thin Ag layer in the liquid solder.

10.4.II. *Metalizing Glass by the Burning-in Technique, Using So-called Metal Lusters*

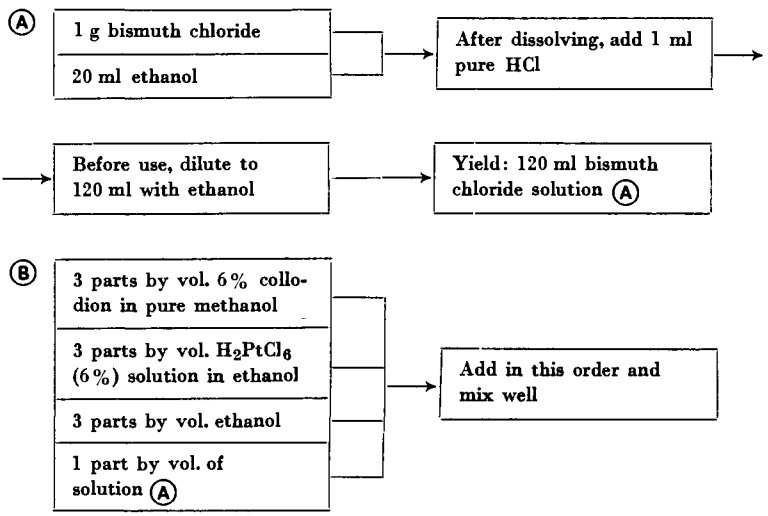
This process is specially suited to firing-on layers of Pt, for glass, quartz, and glazed or unglazed ceramic substrates. The carefully cleaned, and in particular degreased, surface is thinly brushed, sprayed or stamped with a solution of chloroplatinicacid (H_2PtCl_6) in alcohol, and containing oil. This is sold under the name "platinum bright"; it is made by such firms as HERAEUS-PLATINSCHMELZE, Hanau, JOHNSON and MATTHEY, England, and DEUTSCHE GOLD- UND SILBERSCHEIDEANSTALT (DEGUSSA), Frankfurt am Main. (The last-named supplies a special product "Poliersilber 242 L", which is applied by brush in thicknesses of 5–40 g/100 cm² glass surface, and is then fired at *ca.* 540° on soft glass, 600–650° on hard glass.) The layer is dried for 10–60 minutes, and then slowly (3.5°/min) heated in a well-vented electric muffle or conveyor furnace in a purely

oxidizing atmosphere, or fired in air over a flame. The highest temperature of firing is set by the type of glass and its softening point; for soft soda-lime glass *ca.* 500–550°, for hard borosilicates *ca.* 700°, and for very hard glasses and ceramics *ca.* 900°. The coating first goes brown when heated, then the oil additive evaporates, and a metallic mirror surface appears that initially can be easily wiped off, but at elevated temperatures sinters firmly to the glass to make a layer about 1 μ thick.

If the layer is too thin after one coating, the process can be repeated; in this way, Pt layers 50 μ thick can be made, whose adhesive strength is 1.5–2 kg/mm² (UMBLIA).

According to a well-known recipe by KUNDT, "platinum bright" can be made by [10.4] dissolving 1 g H_2PtCl_6 (often incorrectly called platinum chloride) in 3 ml absolute

TABLE T 10–24. RECIPE FOR MAKING "PLATINUM BRIGHT" ([15]ANON., ANGERER)


Ⓐ
1 g bismuth chloride
20 ml ethanol
After dissolving, add 1 ml pure HCl
Before use, dilute to 120 ml with ethanol
Yield: 120 ml bismuth chloride solution Ⓐ
Ⓑ
3 parts by vol. 6% collodion in pure methanol
3 parts by vol. H_2PtCl_6 (6%) solution in ethanol
3 parts by vol. ethanol
1 part by vol. of solution Ⓐ
Add in this order and mix well

alcohol, or according to PARTRIDGE 35 ml, with addition of 10 ml concentrated alcohol solution of B_2O_3, and 20 ml Venetian turpentine and lavender oil (equal parts of each). The rather viscous solution can be stored indefinitely, but attacks cork stoppers. Uniform mirror surfaces can be made by avoiding the oil additive ([15]ANON.), and adding bismuth chloride (see Table T 10–24). HERITAGE, [2]MONACK, PARTRIDGE, and UMBLIA give other recipes.

In a similar way, Au, Ag, Ir, and Pd layers can be made with corresponding solutions as carriers, and are marketed under the names "gold bright", "silver bright", etc. The compositions are essentially more complex than that for Pt (see RUSSEL for detailed recipes), so that in general they do not lend themselves to "do it yourself" procedures. Such commercial metal lusters include, besides the noble metals, Bi, Cr and Rh; the last metal appears to contribute to particularly good coatings even when the amount of metal is only a few parts per thousand of the quantity of noble metal. RUSSEL states that a good commercial platinum bright ("Glanzplatin Ia", of DEGUSSA) contains 5.60% Pt, 2.34% Au, 0.33% bismuth oxide, 0.05% Rh and 0.033% chromia.

A simple process for paint-and-sinter silvering of glass is as follows: Ag_2CO_3 can easily be made from the nitrate and K_2CO_3 in aqueous solution:

$$2AgNO_3 + K_2CO_3 + H_2O = Ag_2CO_3 + 2KNO_3 + H_2O.$$

The carbonate precipitates and the nitrate remains in solution Ag_2CO_3 are then dried, 2–5% terpineol and oil of turpentine is added and mixed in a mortar to a paste of the consistency of thin honey. Terpineol is not required if aged, partly resinified oil of turpentine is used. The glass is then coated evenly with paste by dipping or painting, and waved continuously over a hot-plate at a medium temperature to smoke off the oil. [10.4] Care must be taken to avoid too strong heating which forms bubbles. The original olive green now changes rapidly to dark brown as silver oxide forms. When no more oil smoke comes off, the layer is "white-fired" in a Bunsen flame characterized by a gentle "roaring" sound; metallic silver being formed by this process. When cooled, the outlines of the silvered surface can be drawn lightly in with a razor blade or suitable knife. Next, the layer is reheated up to the point where the glass just begins to glow. The resulting Ag layer is matt gray-white, and can be polished with alumina or a buffing wheel. It is exceptionally adherent, can be soft-soldered, and is so chemically resistant that it is not damaged even by a short exposure to cold concentrated HNO_3 (OEHME).

Noble metal layers made by the burning-in technique can be soft-soldered to other metals (see 10.4.II–VI above). Very thin layers on the inside of glass or ceramic tubes, needed to prevent electrostatic build-up, can be made by diluting commercial lusters with acetone before application and firing.

10.4.III. *Chemical Silvering of Glass*

(ANGERER, GARDNER, HERITAGE, KOHLRAUSCH, LUX, [2]MONACK, STRONG, UMBLIA, WEHNELT, WEIN, [4]WEYL)

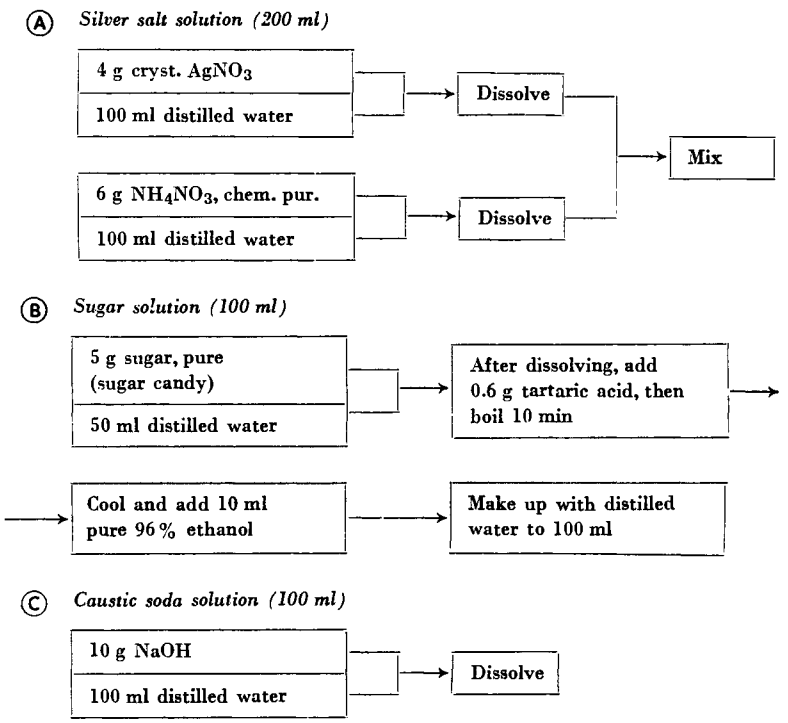
All methods of this type consist of precipitating Ag from ammoniacal silver-nitrate solutions by means of a reducing solution. Among the best-known are three methods, the formaldehyde, the Seignette salt or Rochelle salt, and the sugar method, and many variants of each are used in practice. A few simple recipes follow:

(a) *Formaldehyde method:* 8 g crystallized $AgNO_3$ are dissolved in 100 ml distilled water and ammonia is added dropwise until the precipitate formed has *almost* disappeared. The color should be gray-yellow, with no excess ammonia, or there will be no mirror deposit. If the solution goes too clear, add $AgNO_3$ solution. See STRONG or ANGERER for exact procedure. The solution is then filtered, and must be stored in dark-brown glass-stoppered flasks. Shortly before use, about 50 drops of 30% formaldehyde should be added. In this bath (20°) the glass parts should be laid; they should be filled with the solution if internal silvering is desired.

(b) *Rochelle salt method* (SIMON), specially suited to internal silvering of photocells. This method has possible variations discussed by ANGERER and by HEPBURN. Solution I: 5 g $AgNO_3$ in 100 ml distilled water, add ammonia clarifier as in (a), then add further 400 ml of distilled water and store in a dark flask. Solution II: 1 g $AgNO_3$ in a little distilled water, then add 500 ml boiling distilled water and add to that 0.83 g Rochelle salt (sodium potassium tartrate); let the solution simmer and, while still hot, filter off the gray precipitate; the solution will keep for about one

month in a dark flask. Before use, both solutions are mixed in equal parts at room temperature and immediately poured into the photocell. The formation of a Ag deposit is slower than with (a) and may take an hour, after which decant the liquid. Quantities given suffice for a rugged Ag film on a 200 cm^2 area. If the mirror is too thin, the process can be repeated with fresh solution after a short rinse in distilled water.

TABLE T 10-25. RECIPES FOR SOLUTIONS USED IN MAKING Ag LAYERS ON GLASS BY THE SUGAR METHOD (KOHLRAUSCH) [10.4]


Ⓐ Silver salt solution (200 ml)
4 g cryst. AgNO3
100 ml distilled water
Dissolve
6 g NH4NO3, chem. pur.
100 ml distilled water
Dissolve
Mix
Ⓑ Sugar solution (100 ml)
5 g sugar, pure (sugar candy)
50 ml distilled water
After dissolving, add 0.6 g tartaric acid, then boil 10 min
Cool and add 10 ml pure 96 % ethanol
Make up with distilled water to 100 ml
Ⓒ Caustic soda solution (100 ml)
10 g NaOH
100 ml distilled water
Dissolve

(c) *Sugar method* (KOHLRAUSCH): variations by ANGERER and by HEPBURN. Three solutions are made according to Table T 10–25, a silver solution *A*, a sugar solution *B* and a caustic soda solution *C*. For silvering, 15 ml of *B* are poured into 30 ml of *A* and 15 ml of *C* are added. This avoids the chance of explosion from silver fulminate formation which may occur with similar recipes. Reduction begins when *C* is added and the deposit is complete after 25 minutes at 20–22°. The fluid should be swilled about during this period.

The result of all such methods depends strongly on the purity of the reagents and the cleanliness of the vessels, and particularly on the cleanliness of the glass surface to be silvered. Glass-cleaning methods for the latter case are given in 10.4.Ie or If, and the best way is to use hot chromic sulfuric acid (10.4.Ig). After cleaning, it is recommended

that the surfaces to be silvered be left in distilled water. The adhesion of the Ag layer is not very good. Adhesion and rate of deposition are improved by rubbing with a $SnCl_2$ solution + citric acid (ANGERER) before rinsing in distilled water. STRONG recommends a concentrated solution of $SnCl_2$ followed by thorough washing in tap water and distilled water, whereas UMBLIA recommends very dilute solutions. However, the process activates the glass; i.e. the silica gel on the glass surface absorbs Sn ions (Sn^{++}) which, since they have unsaturated valency bonds, accelerate reduction of Ag ions to Ag atoms, so that a mirror forms more quickly on such an activated surface than on
[10.4] an unactivated one. At the same time the adhesion of Ag atoms is increased because the highly polarizable Sn ions are held to the glass by primary valency bonds but appear from the side opposite the glass as neutral metal atoms (no outwardly directed field of force) which assists them to form typical metallic bonds (see, e.g., BOETTCHER, [3,4]WEYL for further details).

Since reduction of Ag ions to metallic Ag takes place not only on the glass but also in the solution, the yield in chemical silvering even of activated surfaces seldom exceeds 20%.

Once reduction is finished, the fluid should be decanted rapidly and the metal layer washed with distilled water. A well-wetted pad of cotton is then used to wipe off loose gray Ag with light pressure under distilled water, provided the mirror is accessible and that this process, which produces high reflectivity, is required. The reflectivity of chemical silvering is very high, and the films may be up to 10 μ thick. (A layer 0.3 μ or 3×10^{-5} cm thick is enough to give a good mirror; see Fig. B 10-214A.)

If such mirrors are applied to the inside of vacuum tubes, they should be freed from H_2 and H_2O by initial outgassing at 150° at least, on the oil diffusion pump. When external silvering is applied (as in reflector lamps), the mirror should be Cu plated (see HEPBURN for suitable recipes) and then lacquered immediately after it is made and has been washed in distilled water, but without drying first. If the thermal and mechanical stresses are low, a protective layer of bronze lacquer is sufficient. HERITAGE gives special recipes for silvering, coppering and nickeling thin metal layers deposited on glass, ceramics, etc. Thickening by electrodeposition must take place at once after the substrate metal film has been made; avoid dipping the metalized parts in an electroplating bath when no current is flowing.

As a rule, only Ag layers are applied to glass by the chemical methods described, but Cu (FRENCH, [2]MONACK, UMBLIA), Au (GIBSON, [2]MONACK) and Ni films ([2]MONACK, UMBLIA) can also be made similarly (see also [4]WEYL).

In HV technology, these chemical methods have been replaced to a large extent by vacuum evaporation of metals.

10.4.IV. *Metalizing Glass Surfaces by Cathodic Sputtering*

(ANGERER, [16]ANON., BELSER, GÜNTHERSCHULZE, HEPBURN, [6]HOLLAND, HULBURT, [1]KEYWELL, [1]KNOLL, MASSEY, [1,2]METHFESSEL, MÖNCH, STRONG)

The process arises from the fact that the metal surface of a cathode in an abnormal glow discharge sputters considerably (gas-filling $1–10^{-2}$ Torr, cathode–anode gap 5–10 cm, D.C. operating voltage 1–5 kV with series load resistor, discharge current 5–50 mA). This is because bombardment by gas ions heats the surface locally to the

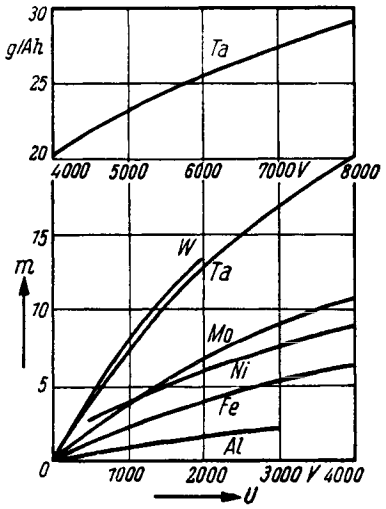
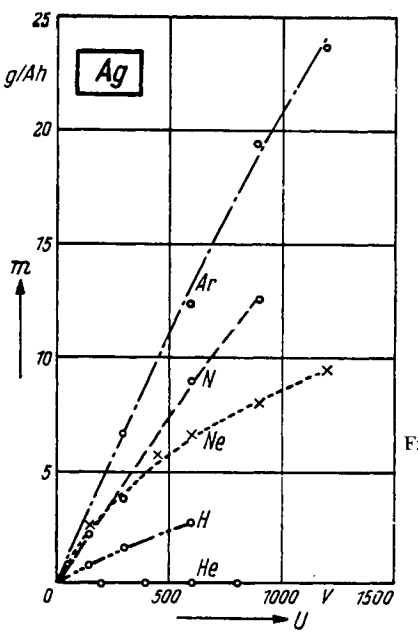


Fig. B 10-196 Cathodic sputtering m of metals in Hg vapor at 18° as a function of tube voltage U (GÜNTHERSCHULZE)

Ion production by auxiliary discharge, cathode–anode gap 2 cm, cathode surface 16 cm², current 10 mA, low-voltage values for Ni unreliable



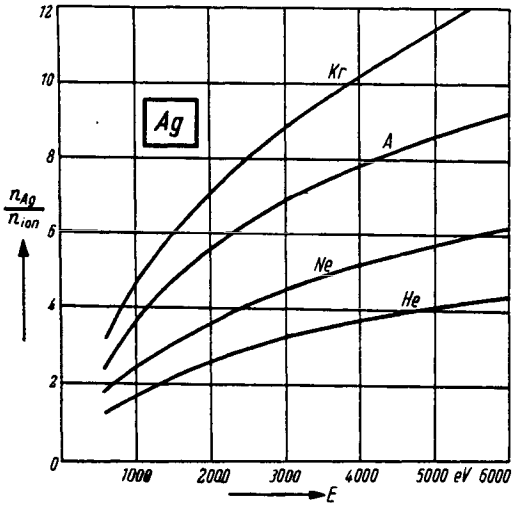


Fig. B 10-197A Sputtering of Ag in noble gases (KEYWELL)

Ratio of sputtered Ag atoms n_{Ag} to inert gas bombarding ions n_{ion} as a function of collision energy of ions E for different gases

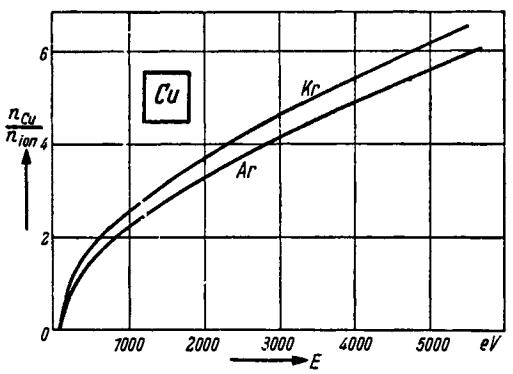


Fig. B 10-197B Sputtering of Cu in inert gases (KEYWELL)

Ratio of number of sputtered Cu atoms n_{Cu} to number of inert gas bombarding ions n_{ion} as functions of ion collision energy E for various gases

Fig. B 10-197 Cathodic sputtering m of Ag sheet in various gases as functions of tube voltage U (GÜNTHERSCHULZE); ion production by hot-cathode auxiliary discharge to anode, mean free path of all gases = that of Ar at 0.01 Torr, cathode surface 22.5 cm², cathode temperature *ca.* 530°, anode–cathode gap 2.5 cm, current in discharge 20 mA

[10.4]

point where metal atoms evaporate, form a dense space-charge cloud round the cathode as they lose energy by collisions with the filling gas molecules, and thence diffuse to cool surfaces, including, unfortunately, many to the cathode which as a whole remains cool if the current is not too great. Condensation occurs at the cool areas. If now a glass plate is placed near the cathode, and its diameter is somewhat less than that of the cathode, it will be coated with a uniform metal layer; it should not be brought so near that the discharge is interfered with, i.e. it should be a little beyond the cathode dark space and preferably as parallel as possible to the cathode surface.

[10.4]

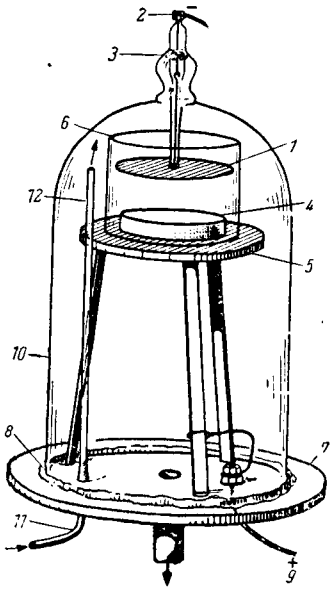


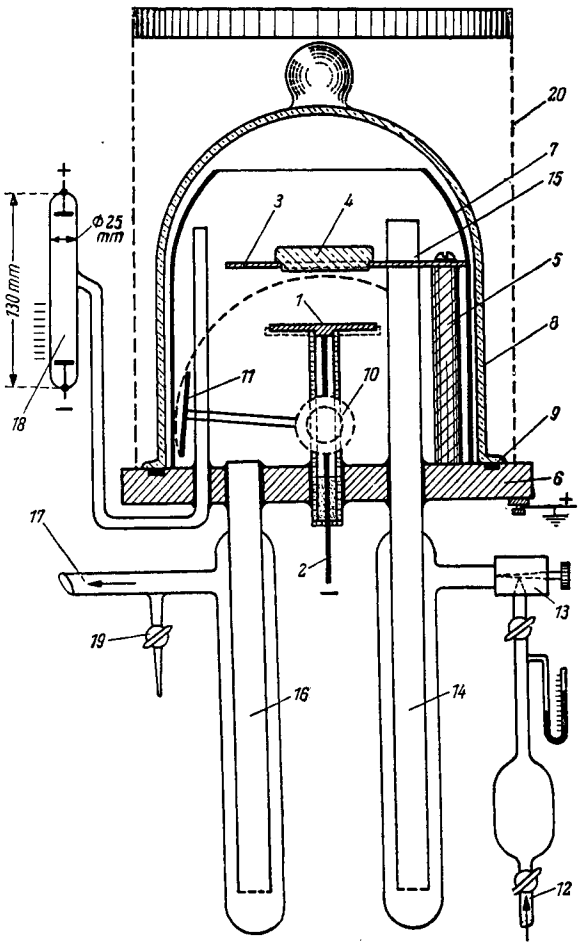
Fig. B 10-198 Simple glass apparatus for metalizing glass plates by cathodic sputtering ([1]STRONG)

1 cathode disk covered on reverse side with glass or ceramic disk; *2* cathode lead (—1000 to —5000 V); *3* Apiezon wax joint; *4* plate to be metalized; *5* Al support plate; *6* hard-glass cylinder to protect bell-jar from deposition; *7* base-plate of metal (Fe or tinned brass) or of glass; *8* Apiezon wax or rubber seal (no grease); if rubber, the bell has thickened plane-ground flange; *9* anode lead (+1000 to +5000 V); *10* thick-walled glass bell-jar; *11* filling gas inlet (metal capillary); *12* glass tube extension of gas inlet

The process as sketched above (see also WEHNER) makes it clear that the amount of metal sputtered—apart from initial reactions—increases linearly with discharge current and time, and with collision energy, i.e. with operating voltage and the mass of the gas ions. (See Figs. B 10-196 to B 10-197B.) It also explains how in sputtering of alloys the difference in VP of the constituents plays no essential part, in contrast to HV evaporation. Sputtered alloys have almost the same composition of deposit as had the original bulk alloy.

Figure B 10-198 shows a simple sputtering apparatus of the classical type, Fig. B 10-199 a glass unit for more exacting requirements, and Fig. B 10-200 a simple apparatus with metal envelope and water-cooled cathode which will make an opaque (10^{-5} cm) film of Au or Ag inside 10 minutes. Further constructions of sputtering apparatus are given by [5]ANON., BLECHSCHMIDT, [1]CARTWRIGHT, FRUTH. Figure B10-201 shows a modern commercial version of a complete sputtering unit. As the process produces even and uniform layers on the side of the cathode opposite the anode although the yield is small, commercial equipment is often made with the surface to be coated placed, not between anode and cathode, but behind the cathode. The latter is

therefore naturally mounted in the discharge space on supports at the rim, not by a central rod. If cost prohibits making the cathode material out of the solid to be sputtered,



[10.4]

Fig. B 10-199 Glass apparatus for cathodic sputtering in a flow of Ar (similar to ANGERER design)

1 cathode screened on reverse side by ceramic plate, possibly also water-cooled internally; *2* cathode lead, Al shielded with glass sleeve, or enameled Novar, taken via an insulator through the baseplate, test-voltage 15 kV; *3* Al sheet support, acting as both anode and work-holder; *4* work, glass plate; *5* glass-sleeved Al column to support *3*; *6* grounded baseplate of tinned brass, possibly water-cooled; *7* hard-glass to protect bell-jar from deposition; *8* thick-walled hard-glass bell-jar with thickened, ground sealing-flange: *9* ungreased gasket of white vacuum rubber or silastic; *10* rotary silicone-greased ground-joint and arm brought through side of jar to position Al sheet baffle *11* in front of *4*; *12* gas inlet; *13* needle-valve to regulate gas; *14* cold-trap for inlet gas; *15* inner gas-feed tube; *16* cold-trap for pumping line *17*; *18* Geissler tube with Al electrodes for estimating and setting gas pressure, or may be replaced by thermocouple gauge (1–10^{-3} Torr); *19* stopcock to let in dry air for opening up the apparatus; *20* wire-mesh guard

it is electroplated to sufficient thickness with this material (Au, Ag, etc.); the deposit must be pinhole-free and be vacuum-degassed before use. Another technique is to spot-weld a thin foil of sputtering material to the substrate, or use a pure tin solder.

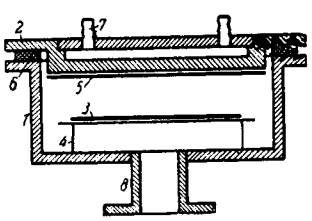


Fig. B 10-200 Metal-chamber sputtering apparatus ([3]KNOLL)

1 anode, and also tank or chamber; *2* cathode, also cover-plate; *3* work; *4* support; *5* source, sheet material, e.g. noble metal, fastened to and in electrical contact with *2*, or electrodeposited on it; *6* rubber gasket, also insulates cathode from anode; *7* watercooling; *8* pumping line and gas inlet

The metal substrate should be well screened by ceramic material. Cathodes made of parallel wires or mesh are suitable for sputtering.

The following fundamental points should be observed in the construction of sputtering equipment:

The cathode shape must be matched to the object to be coated to achieve uniform layers; to metalize a flat surface, a flat cathode disk must be used of diameter somewhat larger than that of the glass disk to be coated, and it must be parallel to it, so that the metal-vapor density gradient is everywhere normal to the receiver surface. To mirror-
[10.4] coat a large number of small glass targets, the latter are laid on one plane carrier plate parallel to the cathode.

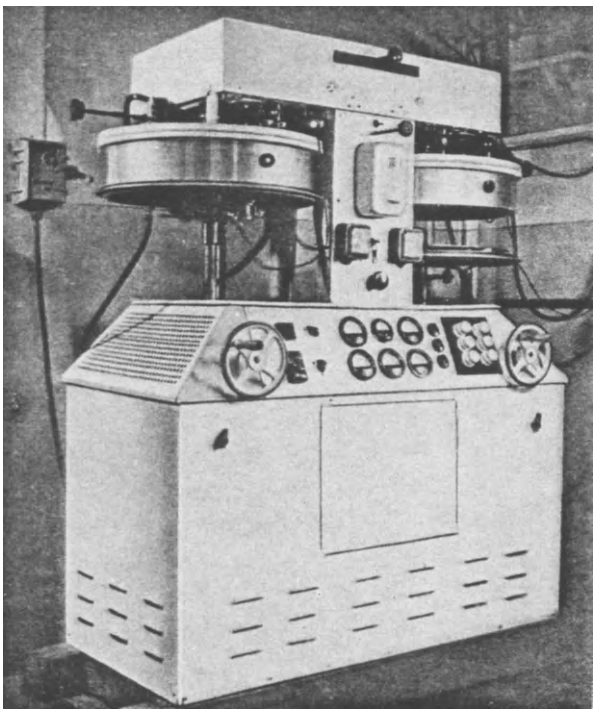


Fig. B 10-201 Research model of dual sputtering plant, made by HERAEUS-LEYBOLD ([2]HIESINGER)

Both sides of a glass disk can be coated by surrounding it with a U-shaped cathode. Central wire cathodes can be used to mirror-coat the inside of tubes, whose lengths should not be much greater than their diameters; cylindrical cathodes are used to metalize the outside of tube or rod. If the cathode plate is large and the discharge currents are high it is necessary to water-cool the cathode internally (see, e.g., Fig. B 10-200), since too large a temperature gradient produces density variations in the filling gas and endangers the discharge. By this means one can get up to six times the sputtering intensity possible with uncooled cathodes. The opposite has also been done, i.e. the cathode is heated, in the case where large numbers of thin wires are used to make it. (The wire diameter is less than the mean free path of the metal atoms in the

filling gas.) This form of cathode has often been chosen where the before-mentioned back-diffusion of sputtered material is to be kept as small as possible by reducing the cathode area; to reduce condensation, the wires are insulated from each other and heated by direct current, which is in addition to discharge current heating. According to RICHTER, this construction permits deposition of 0.1 μ Ag within 2 minutes, whereas a bulk sheet cathode under otherwise identical conditions would require more than 3 hours.

Condensation of sputtered material on cold walls near the discharge makes it advisable not to have too small a sputtering chamber, to avoid both needless loss of metal- [10.4] vapor and reduced density of deposition at the edge of the coated surface. As a general rule, the cathode–wall gap should be at least equal to the cathode diameter.

All cathode connecting leads should be made of low-sputtering-rate material (Al) and be carefully screened by glass sleeves, or enamelled leads should be used. The back of the cathode should be screened by a ceramic, not mica, plate. Mica can decompose and cause contamination. Greased stopcocks should be avoided. If unavoidable, they should be greased with silicone, since hydrocarbon vapors are cracked in the discharge ([7]HOLLAND) and can lead to carbon deposition. The bell-jar seal should be ungreased vacuum rubber or silastomer. To avoid frequent and complicated cleaning of the glass bell-jar, it is recommended that a hard-glass cylinder be provided to protect the jar from deposition (Fig. B 10-199, *7*). Glass bells should always be fitted with external closemesh metal screening to guard the operator in case of implosion.

Literature data on the best cathode dimensions, work–cathode gaps, gas pressures, operating voltages and currents, all differ very widely. In general, the operating voltages lie between 1 and 8 kV, obviously with a stabilizing series-resistance load, and the filling pressure usually lies between 1 and 1/10 Torr, regulated so that the cathode dark space occupies two-thirds to one-half the gap between cathode and surface to be coated. The gap itself is 20–50 mm as a rule. Take the example of a 60 mm dia. glass target to be silvered: the following arrangement would be recommended (PTR); cathode dia. 90 mm, cathode–work gap 43 mm, cathode–anode gap 120 mm, Ar filling, dark space (at 1350 V, 7 mA) 33 mm at start (less at end of deposition process), time for a half-mirror 12 minutes. Another example: Ar filling, 2 kV overall voltage drop (1 kV across the electrodes, 1 kV across the series load), dark space 10–20 mm, cathode–work gap 25 mm, cathode current density 2–3 mA/cm^2.

For clean deposits the following points should be watched: all constructional parts, including the tank or chamber, should be carefully degassed before use, preferably at temperatures of 150–200°. One should work with a flow of pure gas ([2]KNOLL), fed through a needle-valve at about 1 liter (NTP)/hr and pumped continuously away (the pump may have to be throttled) to keep a constant pressure of desired value, and so maintain the cathode space constant. Hg, grease and water-vapor should be trapped out by liquid air on both the gas inlet side and the pump side (see Fig. B 10-199).

The actual sputtering should preferably only begin when the cathode surface layers have been removed by pre-sputtering. During this time the work should be blanked off by baffles (see, e.g., Fig. B 10-199, *10* and *11*).

The glass target surface should be carefully cleaned. A reliable method is to wash it in chromic sulfuric acid (see 10.4.Ig) and rinse in tap water and distilled water.

TABLE T 10–26. CATHODIC SPUTTERING ORDER OF THE CHIEF VACUUM METALS

M = sputtered amount in g/cm² of *cathode* surface and per mA-hr (specific sputtering rate)

m = amount deposited by sputtering in g/cm² *receiving* surface and per mA-hr

d = deposit layer thickness in Å (10^{-8} cm) per mA-hr

CATH. = cathode; MATL. = material

1		2		3		4			5		6		7	
IN H_2 [1]		IN Hg [2]		IN Ar [3]		IN Ar [10]			IN N_2 [4]		IN AIR [5]		IN AIR [6]	
CATH. MATL.	M $\left[\frac{g}{cm^2}/mA \cdot h\right]$	CATH. MATL.	M $\left[\frac{g}{cm^2}/mA \cdot h\right]$	CATH. MATL.	M	CATH. MATL.	m $\left[\frac{g}{cm^2}/mA \cdot h\right]$	d [Å/mA · h]	CATH. MATL.	M	CATH. MATL.	M	CATH. MATL.	TIME TO SPUTTER 10^{-5} cm LAYER
Mg	1.3×10^{-6}	Be	27×10^{-6}	Mg	Low	Al [11]	$(\approx2.5\times10^{-6})$	(≈90)	Ni	Low	Mg	Low	Be	Very hard to sputter
Ta	2.3×10^{-6}	Al	67×10^{-6}	Al		Os [12]	17×10^{-6}	75	Cu		Al		Si	
				Si					Pd		Fe		Mg	
Cr	3.9×10^{-6}	Si	70×10^{-6}	W		Ru [13]	17×10^{-6}	135	Pt		Ir		Cr	
Al	4.2×10^{-6}	Mn	141×10^{-6}	Fe		Ir [14]	67×10^{-6}	300	Au		Ni		Al	
				Ni					Ag	High	Cd			
Cd	4.6×10^{-6}	Fe	144×10^{-6}	Pt		Mo	34×10^{-6}	375			Cu		W	Several hours at 10 mA
Mn	5.4×10^{-6}	Ni	150×10^{-6}	Cu		Ni	48×10^{-6}	510			Pt		Ta	
				Sn							Sn		Mo	
Mo	8.0×10^{-6}	Zr	212×10^{-6}	Au		Cu [15]	47×10^{-6}	525			Ag			
Co	8.0×10^{-6}	Co	215×10^{-6} [8]	Ag		Pt	116×10^{-6}	540			Au		Se	2 hr at 50 mA
				Cd	High						Pd	High	Ir	
W	8.1×10^{-6}	Cr	218×10^{-6} [8]			Rh	89×10^{-6}	720					Co	
Ni	9.3×10^{-6}	Mo	246×10^{-6}			Pd	99×10^{-6}	810					Fe	
													Cu	
Fe	9.7×10^{-6}	Cu	432×10^{-6} [8]			Au	196×10^{-6}	1020					Ni	
Sn	28×10^{-6}	Ta	463×10^{-6}			Ag	158×10^{-6}	1500						
													Sn	1 hr at 50 mA
C	38×10^{-6} [7]	W	478×10^{-6}										Ag	
Cu	43×10^{-6}	Pt	984×10^{-6} [8]										Pt	
													Au	
Au	66×10^{-6} [9]	Ag	1280×10^{-6} [8]										Cd	
Ag	106×10^{-6}													
Te	154×10^{-6}													

Directly before sputtering, the surface should be wiped with a cotton wad moistened with pure ethanol, avoiding dust particles on the glass. [2]STRONG recommends flaming the surface which amounts to moving a torch flame (which is highly ionized) over the surface. It has also proved valuable to heat the glass plate, immediately before deposition, in HV on a hot-plate in the apparatus. The most efficient process seems to be to remove adsorbed gases from the surface by ion bombardment. To do this, the initial pressure during actual sputtering should be reduced to 0.03 Torr, and the electrode potential drop to about 1 kV; the glass plate is bombarded for 3 minutes or so at 150–200% of normal sputtering current density (PARTRIDGE). Only then is the filling [10.4] pressure raised to *ca.* $^1/_{10}$ Torr and ordinary sputtering carried out.

It is very difficult to obtain precise quantitative data on the sputtering rates of different materials. The sputtering intensity depends strongly on the ambient conditions in the apparatus concerned and rarely-controllable chemical processes exert a powerful influence; an example of the latter is the effect of unavoidable impurities in noble gases used in sputtering. The sputtering rates of individual metals are much affected by surface layers, especially oxides and nitrides, which protect the metal from direct impact of gas ions and thus reduce removal of metal. This effect is particularly noticeable with Al, Be, Cr, Mg and Ta, which are well known for their tendency to form adherent oxide layers and therefore practically do not sputter at all in reactive gases. According to [2]HIESINGER, the explanation for the discrepancy between the high sputtering rates of oxidation-resistant and the low rates of oxidation-prone metals may be explained by the fact that even in inert gases the latter readily form oxides on the coated object

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Footnotes to Table T 10–26

(1) GÜNTHERSCHULZE: operating voltage 850 V, cathode fall 770 V, anode–cathode gap 60 mm, cathode area 7 cm², current 40–50 mA.

(2) GÜNTHERSCHULZE: operating voltage 1 kV, anode–cathode gap 20 mm, cathode area 16 cm², current 2–10 mA, Hg temp. 11–15°, auxiliary electron source for ion production.

(3) BLECHSCHMIDT.

(4) KOHLSCH ÜTTER.

(5) CROOKES.

(6) HULBURT: operating voltage 1–2 kV, cathode dia. 50 mm, cathode dark space 50 mm depth, cathode-target gap 20–40 mm, current 50 mA.

(7) Sputtering rate much increased by chemical reaction with the H_2 filling gas.

(8) Effect of amalgamation plays a large part in these resnlts.

(9) This corresponds to a layer thickness of about 3×10^{-6} cm; according to PARTRIDGE, the evaporation of Au in air is 20×10^{-6} $\frac{g}{cm^2}$/mA·hr, corresponding to a layer of about 10^{-6} cm, where the following conditions obtained: 1.2 kV operating voltage, gas pressure 0.1 Torr, current 10 mA.

(10) [2]BELSER (values arranged in order of increasing thickness *d*): $2–3 \times 10^{-3}$ Torr of dry Ar flow, operating voltage 3650 V, cathode-target gap 3–5 cm, cathode dia. (where not otherwise given) 50 mm, current 20 mA.

(11) Cathode rod *ca.* 22 mm dia., 3 kV, 100 mA, *m* and *d* values only approx.

(12) Cathode dia. *ca.* 22 mm.

(13) Cathode dia. 25 mm.

(14) Cathode dia. 38 mm.

(15) With considerable amounts of oxide.

which, because of low light-absorption, are hard to detect, and determinations of the amounts sputtered are falsified thereby. In pure inert gases and Hg vapor, the sputtering rate rises sharply if the oxide is removed. However, even the other metals can only be quantitatively evaluated for sputtering rate on a comparative basis (see Table T 10–26). Numerical results are discorded, and one has to be satisfied with a qualitative order of "sputterability" in a given gas (see Table T 10–26, cols. 3 and 5–7). For approximate evaluation of quantities to be sputtered, use can be made of the facts that Ag or Au layers are opaque above about 10^{-5} cm (0.1 μ) thickness, and are semi-transparent
[10.4] (more properly, partly transparent) at 10^{-6} cm.

Sputtered layers have a crystalline structure; the particles aline themselves in the strong field of the glow discharge and atoms of the filling or residual gases in the apparatus are bonded in the lattice of metal atoms.

Applications. This process is mainly suited to making thin, semi-transparent, electrically conducting layers of metals, and for high-reflectivity mirrors on exposed, wholly accessible surfaces like glass plates, slightly curved mirrors and external surfaces of cylinders, which can perhaps be slowly rotated by electromagnetic devices during sputtering. One is not only restricted to glass, other materials can be metalized, e.g. quartz, ceramics, mica; organic materials like wax or plastic gramophone-record master disks can be coated, in this case to provide a stable conducting layer before Cu-plating. Pt has proved the best sputtering material here since, in contrast to Au or Ag, it does not diffuse into the Cu deposit and so causes no surface roughness. More rarely, sputtering is used to apply internal mirrors to envelopes or bulbs. The process is specially suited to making layers of Pt, Ir, Ru, Os and Mo, i.e. metals which are hard to evaporate in high vacuum (see 10.4.V). A flow of H_2 is satisfactory but a flow of oxygen-free Ar is better though more expensive (ANGERER). The adherence of partly transparent films of Pt and Rh can be enhanced by presputtering with Al, Mg or Si ([1]HIESINGER). Sputtering is a better way of making Rh mirrors than HV evaporation. In the special case of Rh a cathode fall of at least 50 mm at 3 kV sputtering voltage is the optimum recommended ([1]HIESINGER).

Assuming correct procedures, the main advantages of sputtering as against HV evaporation of films are generally better adherence to glass or quartz substrates and higher resistance to heat-induced structure changes ([2]BELSER). The main disadvantages are high gas content of sputtered layers and slow rate of deposition.

Cathode sputtering is generally used for:

(a) thin metal films of materials difficult to make by evaporation in HV (as stated);

(b) production of low but precisely adjusted film thicknesses;

(c) deposition of metallic layers on substrates which can only withstand low temperatures, and which therefore must not be exposed to radiant heat from evaporation sources necessary in HV evaporation (see 10.4.V).

For these reasons, cathodic sputtering has proved to be the best way of making light-transmitting electrodes of the order of 10^{-6} cm of Cd and Au on laminar Se photocells, with Ar as filling gas. Optically transparent Au layers on glass exhibit surface conductivity only above 40 Å thickness. If the Au deposit follows after production of a very thin bismuth oxide layer on the glass, the Au need only be 15–20 Å for the same

result ([16]ANON., I. S. PRESTON). At thicknesses of 80–90 Å, such Au films have surface resistivities of only 8–10 Ω/square and optical transmissions of 75–80%. A very thin bismuth layer on top of the Au improves the conductivity and also serves as a protective film. The process is also well suited to making extremely transparent conducting metal, films on glass; see [4]HOLLAND for further details.

Other applications proved in practice should be mentioned:

(a) manufacture of high resistances of low temperature coefficient by sputtering Pt on highly insulating substrates, such as amber (KRÜGER); and Os for high-ohmic sliding-contact resistors; [10.4]

(b) metalizing quartz oscillator crystals with Au, Rh or Pt;

(c) making transparent metal layers for conducting away wall-charges on dial glasses of electrical instruments, and also, for the same reason, on the outside of glass for fluorescent lamps and Hg-vapor rectifier side-arms.

See, e.g., [4,5,6]HOLLAND for making thin conducting metal *oxide* layers (esp. CdO, SnO_2, In_2O_3, Fe_2O_3 and Bi_2O_3) on substrates such as glass, by sputtering in 50/50 Ar/O_2 mixture at 10^{-2} to 10^{-1} Torr.

See 10.4.V, for making protective layers on sputtered mirrors to prevent corrosion.

Cathode sputtering as a harmful phenomenon in the use of so-called "cold" cathodes is treated in Chapter 26.

10.4.V. *Evaporating Metals onto Glass in HV*

(ANGERER, CALDWELL, [15]ESPE, GREENLAND, HEPBURN, [6]HOLLAND, GODLEY, [2,3]METHFESSEL, [2]MONACK, MORAVEC, [1]STRONG)

In this process one can apply, in relatively short times, metallic and nonmetallic layers up to 1–20 μ thick not only to glass, ceramics or mica, but even to paper and plastics, without heating the object to be coated. For the sake of a uniform presentation and to avoid repetition, the treatment here will include evaporation of such metals as are not applied, or not preferentially applied, to glass, but to quartz, ceramics, mica and even other metals.

High vacuum is employed because the composition and pressure of any residual gases much influence the structure and purity of deposited metal layers, and at the start of evaporation at least 10^{-5} Torr is required. The evaporant is heated until its vapor pressure is about 10^{-2} Torr, and it does not matter whether the metal is molten, as it usually is, or whether it is still solid. According to the equation for evaporation rate W (see Vol. 1, 9.5–4), the material comes off at $5–50 \times 10^{-5}$ g/sec/cm^2 of surface. The evaporant atoms, unhindered in HV by collisions with gas molecules, travel in straight lines from the source and are deposited on any object, such as a glass plate, which lies in their path, with a thickness that increases linearly with time.

Any metal that remains below its M.P. at vapor pressures around 10^{-2} Torr, i.e. sublimes, can be heated by direct current passage through wires or (better) strip of the material and so raised to evaporation temperature; radiation shields cut down the heating power required and can be used to beam the evaporant (Fig. B 10-202).

In most cases, however, the evaporant metal is liquid at the necessary temperature and therefore demands an auxiliary heater. The heater should be of a material that

has no significant VP at the temperature of evaporation, nor reacts appreciably with the source material, so as to come over with it or form low-melting alloys which can lead to heater burn-out. Most heaters are of W, Mo, Ta, Nb, or in exceptional cases Fe, Ni and Chromel (composition see Table T 10–27, footnote 4). Figure B 10-203 gives a survey of proven forms and arrangements of heater; where the evaporant wets the heater and to some extent adheres to it (e.g. Al on W), one can use U-shaped wire (*a*) or a waved wire (*b*) or a multi-turn coil (*c*). The evaporant is suspended on these in the form of bent wire or strip (*d*) or as straight rods or zig-zag strip inserted in the heater
[10.4] coil (*e*). The disadvantages of the latter arrangement are that the evaporant shorts out a large part of the heater before melting, and the general thermal contact is often poor so that sections of the heater free of wire charge must be greatly overheated, especially for evaporation temperatures above 2000°, so it is possible that some heater material will evaporate. In such cases, the recommended procedure is to wind the evaporant in

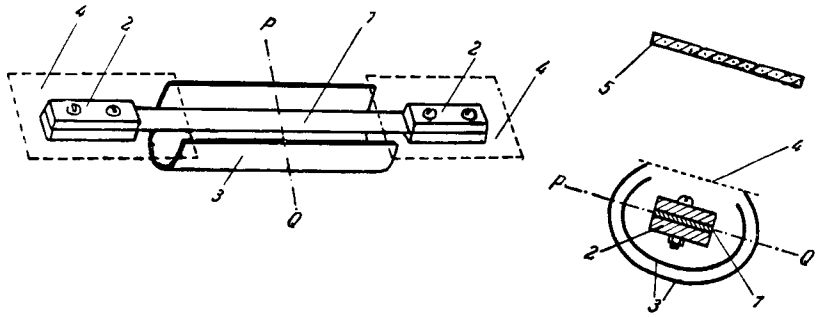


Fig. B 10-202 Evaporation of metal from the solid state by direct heating; used for such metals as Cr, Fe, Ti

1 evaporant metal, preferably strip; *2* thick connexions, possibly water-cooled; *3* Mo sheet screen, possibly two thicknesses; *4* shield against evaporation from leads; *5* glass substrate

the form of fine wire on the heater (Fig. B 10-203, *f*). If only small amounts are to be evaporated, and particularly if precise quantities are involved, the heater can be carefully pickled and then electroplated with evaporant; examples: Ag on Mo, or Cd on W. Pre-plating the heater with evaporant will often improve the adherence of larger amounts of the same evaporant, which can be added in the form of U-shaped riders; an example is Ag suspended on silver-plated W.

When the heater temperature is raised, the evaporant first melts below its evaporating point and, if it wets, runs to the lowest parts of the heater without falling off, and there forms drops (*g*). To prevent these drops reaching the cooler, clamped portions of the heater, the latter are usually arranged to be higher than the rest of the element, (*a*) to (*f*). Further increase in heater temperature will start the evaporation, which will not take place from the center of the drop since this region has a larger diameter and is therefore cooler. Evaporation will proceed from boundary zones (* in (*g*) of Fig. B10-203) between the drop and uncoated incandescent heater. Generally, when the evaporant adheres well, there is a certain degree of reaction (though it may be small) with the heater. A typical example of this is Al on W wire, where the W can dissolve Al up to 3%

or so. This is safe provided large-diameter W wire is used; the rough rule is to have at each section of the heater about three times as much heater material as evaporant. (YARWOOD has made the interesting point here that thoriated W is much less attacked by molten Al than is pure W.) In practice W-wire diameters are from 0.8 to 1 mm and correspondingly heavy Cu clamps and leads are chosen that will not overheat and evaporate with the source.

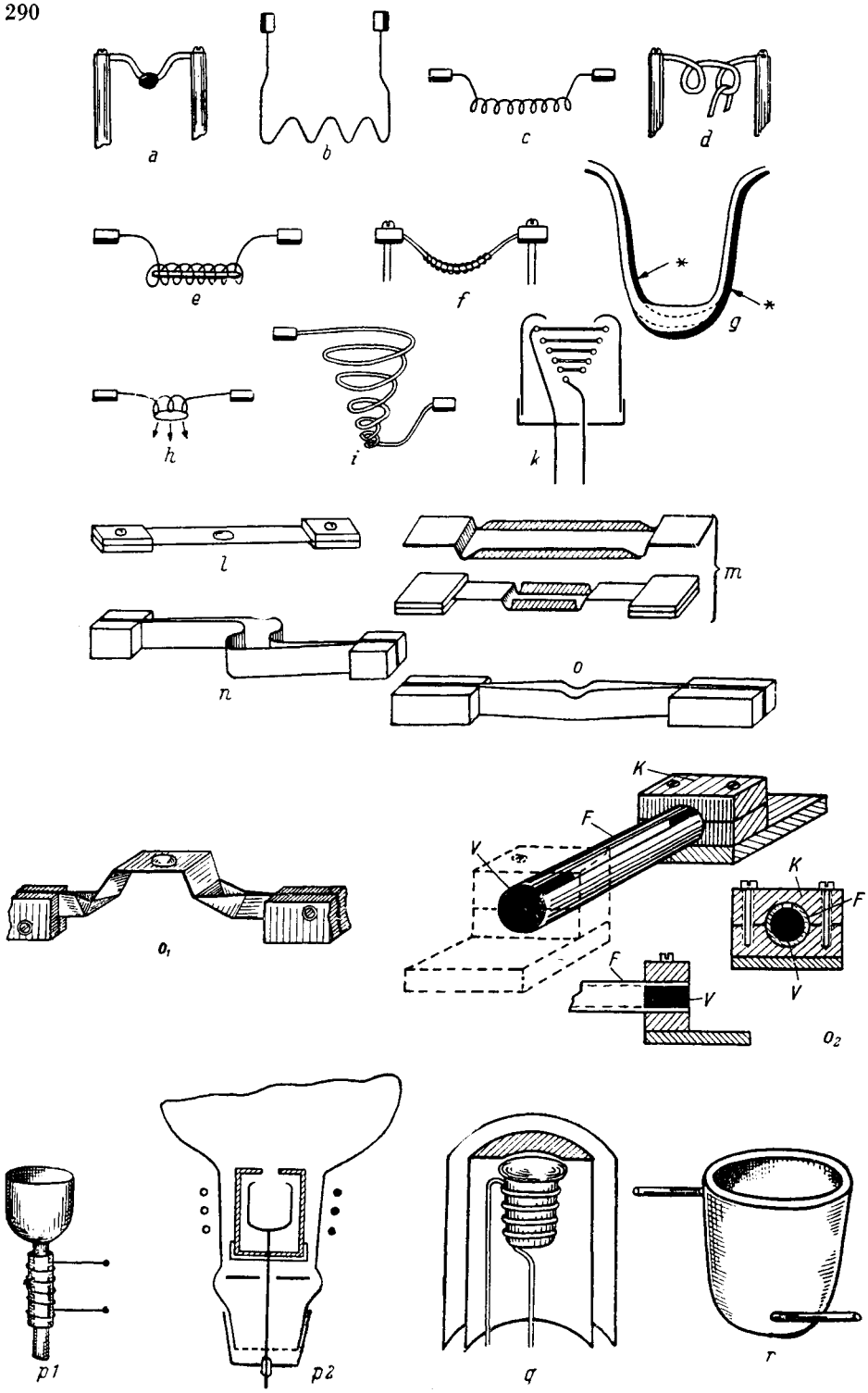
Where the heater is not wetted by the evaporant, e.g. Ag on W, heaters like that in Fig. B 10-203 (*e*) can be used; they are very close-wound thin-wire coils. Surface tension of the molten evaporant prevents run-off (*h*). A still better device is a close-wound wire [10.4] coil with axis vertical, and whose turn diameter decreases to form a cone with apex downwards (*i*). This acts as a holder for the pieces of source metal that hang from the coil windings as molten drops. This type of cone heater can also be enclosed in a combined radiation shield and directional cylinder for beaming the molecules (*k*). A very useful heater for non-wetting sources is a twist of several single wire strands one of which is evaporant metal; for example, 3 W wires and 1 Pt wire, each 0.5 mm dia. This can itself be coiled and maintains a high rate of evaporation without evaporant dropping off.

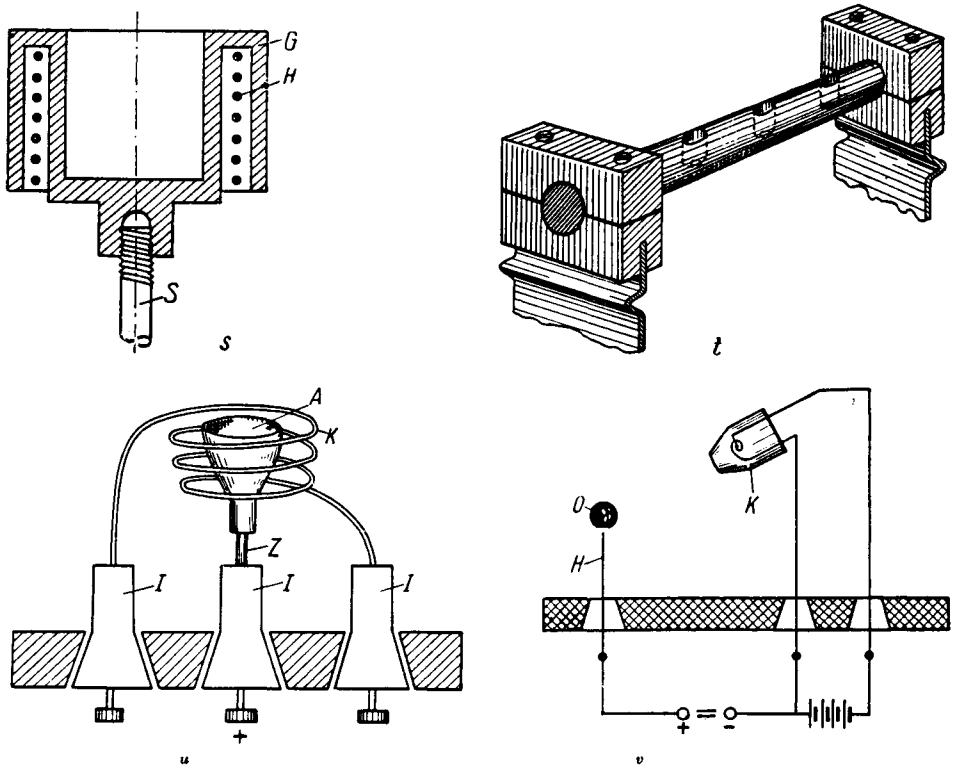
Electrically-heated boats or crucibles must be substituted for the previous heaters when evaporating either large amounts of metal, or powders. An example of the first is the coating of long strips, fed past the source by rollers in the vacuum system, as in metalizing capacitor paper. The heaters for such purposes are either directly heated (D.H.) metal strips suitably shaped as in Fig. B 10-203 (*l*) to (o_2), seamless crucibles of Ta or Mo heated by a coil insulated from the support-post (p_1) or by an H.F. work-coil external to the bell-jar (p_2). (H.F. coils inside the vacuum system are not recommended since the high VP of evaporant may lead to short-circuiting discharges between coil turns, cf. 9.2.II.) See 8.2 of Vol. 1 and Chapter 27 (Flash getters) for evaporation, particularly of alkali earth metals on inner glass surfaces of electron tubes by H.F., where the source metal is mounted on metal plates or rings in the form of a filling in a small-bore metal tube shorting the ends of a wire loop.

In equipment for continuous evaporation of Al on to bulk articles such as paper or plastic strip, success has been achieved with *non-metallic* boats which still conduct electrically and resist attack by Al. Titanium and zirconium carbides have been used, and may be fed continuously with evaporant during the process (ROSS).

Crucibles of glass, quartz or ceramic will evaporate low-melting materials; they are wound with a heater coil and may be provided with a perforated shield to prevent deposition of evaporated crucible material (*q*). Crucibles for materials requiring higher evaporation temperatures, but less than 1600°, can easily be made for oneself as follows: a close-wound W spiral cone (*i*) is painted several times with an alcohol slip of Al_2O_3 powder, possibly with cellulose nitrate addition to act as binder; the coating is dried after each application. The crucible formed (*r*) is then slowly heated *in vacuo* to 1200–1500° and sintered for 5–10 min (OLSEN). For evaporation temperatures above 1800°, a slip of BeO powder in slightly acid water (pH = 1.2) can be used in the same way, but such crucibles crack readily. Another type of crucible made in the same way involves an aqueous thoria slip, made from a 0.1% ThCl solution, and sintering is carried out *in vacuo* at 1700° ([2]CARTWRIGHT). Solid ThO_2 crucibles (i.e. not formed on wire turns), with a flange at the top edge to prevent them slipping out can be dropped into fitting

[10.4]





[10.4]

Fig. B 10-203 Examples of construction of the chief evaporation sources[1]

a U-shaped heater wire; *b* wave-shaped heater wire; c coiled heater; *d* heater coil loaded with evaporant in form of wire hook; *e* heater with insert of rod or folded foil of evaporant metal; *f* heater wound with fine wire evaporant; *g* section of heater after the evaporant metal has melted and wetted; *h* close-wound heater with low-melting non-wetting evaporant metal, which is prevented by surface tension from dropping off; *i* spiral heater; *k* conical heater with radiation screen with vapor-beaming tube and drip-catcher; *l* strip for direct heating by current passage, with embossed hollow for evaporant; *m*, *n*, *o*, o_1, various evaporation boats, D.H.; o_2 rolled D.H. foils as boats (*F* foil, *V* metal end-plug, *K* metal clamps); *p* seamless metal sheet crucible; p_1 heated by thermal conduction; p_2 with ceramic diaphragm, H.F. heating; *q* ceramic crucible heated by radiation and conduction, inserted in heater coil and with two coaxial radiation screens; *r* crucible made by depositing Al_2O_3, BeO or ThO_2 slip on a conical heater of type *i*; *s* graphite crucible, I.H. (*G* graphite, *S* support rod, *H* alumina-insulated Ta heater wire); *t* D.H. graphite rod with radial holes drilled to take evaporant; *u* set-up of crucible for electron bombardment heating (*K* hot cathode, *A* graphite or Ta crucible connected as anode, *Z* lead and support, *I* insulators); *v* electron focal-spot heating (*O* ball of evaporant or carbon, *H* thin W wire support, *K* hot cathode with WEHNELT cylinder from an X-ray tube)

[1] *Note added in German proof:* many other constructions of vapor sources can be found in the recent book by [4]HOLLAND; see also [8]HOLLAND and KELLY, J. C., for electron bombardment heating.

coils of W (*q*) and used up to 2200°; Mo sheet radiation screens are recommended here also.

Graphite is the only heater or crucible material useful for very high evaporation temperatures. The evaporant can either be dropped into holes drilled in the D.H. rod (*t*), or I.H. Graphite crucibles can be used (*s*). However, very large heating currents are needed (400–1000 A), and electron bombardment is also employed, the arrangement being detailed in (*u*). A 4 kV, 100 mA source will produce temperatures up to 3500° in a graphite

crucible in a coaxial W coil cathode, and this will evaporate even W or Mo. However, the crucibles must often be replaced because of metal carbide formation. The high gas-content of graphite also makes difficulties in vacuum work, especially since it takes up gas every time it is exposed to air. Ta is preferable as a crucible material for electron bombardment heating up to evaporation temperatures of 2500°. Very high local temperatures can be achieved by electron bombardment in the focal spot of an X-ray tube's hot cathode (Fig. B 10-203, (*v*)). The electron beam is directed at a solid piece of the evaporant fixed to the end of a thin W wire; anode voltages of 2–5 kV, focal spot
[10.4] areas of 2 mm² and electrode currents of 10–50 mA will, without melting the whole target, produce temperatures high enough to evaporate carbon itself. See ARDENNE on small evaporation furnaces for production of vapor densities required for the ionization space of mass spectrometers, and for isotope separation.

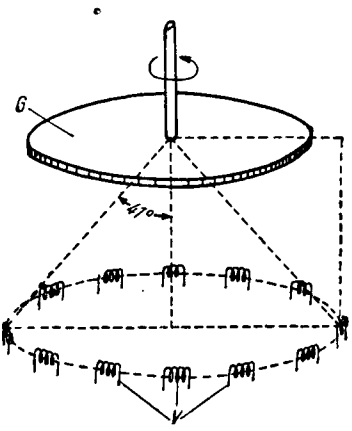


Fig. B 10-203 A Arrangement of vapor sources (*V*) in vacuum coating of very large glass target (*G*) to produce uniform metal deposition; *G* rotates in its own plane during the coating process

With the great importance that vacuum evaporation of metals has won in recent years, there have appeared in the literature many descriptions of laboratory equipment designed for evaporation, most of them of the vertical chamber variety. A controlling factor in all constructions is the fact that the metal deposit is only really uniform in thickness if the source-target gap is much larger than the target diameter. Uniform deposits on large glass surface areas can, however, be made by using one or more point sources at angles of 41° to the surface normal of the target (Fig. B 10-203A) and arranged on a circle whose plane is parallel to that of the glass targets, which should rotate in its own plane while evaporation proceeds. By having rotating diaphragms with specially shaped apertures, large targets can be uniformly coated with metal layers ([1]STRONG).

Figure B 10-204 shows a relatively simple laboratory apparatus with metal vacuum chamber and several separate evaporating coils and a rod-shaped central glow discharge electrode whose function will be referred to below in more detail. Figure B 10-205 gives a schematic illustration of laboratory equipment with a vertical glass bell-jar, a magnetic device for turning the glass target or for rotation of glass cylinders, a large-area discharge electrode and a screened vapor source which can be completely blanked

off during the initial degassi..g process. Figure B 10-206 shows a somewhat simpler arrangement for evaporating glass mirrors, and is distinguished by the special construction of the annular glow discharge electrode (4), which is screened.

[10.4]

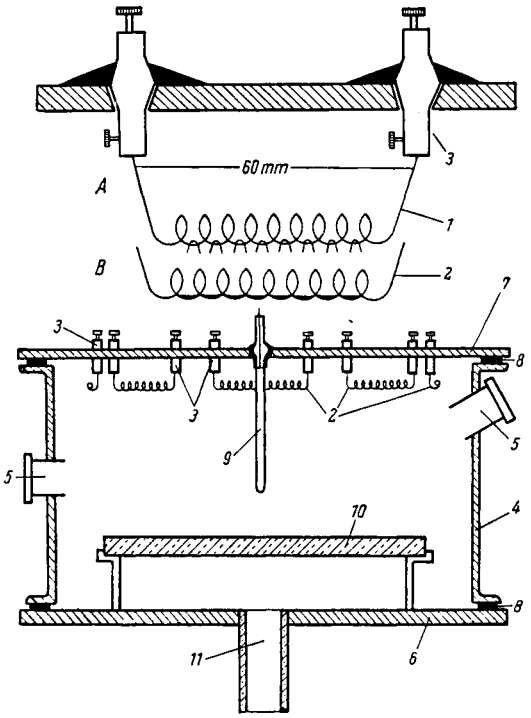


Fig. B 10-204 Laboratory evaporation equipment with metal chamber (YARWOOD)

1 heater for vapor sources (W wire dia. 0.5 mm, coil dia. 6 mm) loaded with Al wire riders of 10 mm length and 0.5 mm dia.; *2* after fusing the evaporant; *3* vacuum-tight insulator bushes; *4* cylinder of enameled steel as vacuum chamber; *5* sight glass; *6* steel baseplate; *7* steel cover-plate; *8* rubber gasket; *9* glow-discharge electrode rod, Al; *10* glass target; *11* pumping line

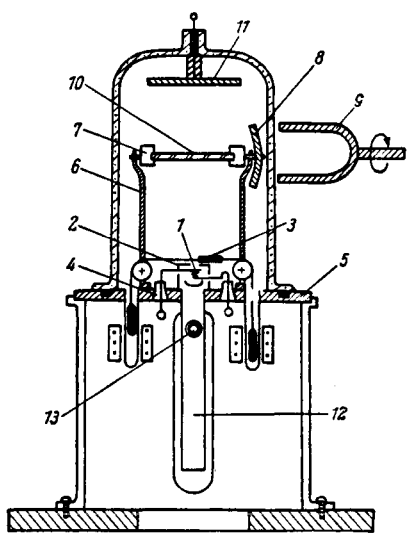


Fig. B 10-205 Laboratory evaporation equipment with glass bell-jar

1 conical W heater coil (cf. Fig. B 10-203, *k*); *2* Mo radiation shield; *3* magnetically controlled baffle plate for source; *4* insulated heater leads; *5* metal baseplate; 6 support device, electrically connected to *5*; *7* supports which can be rotated on axial bushings; *8* Fe rod; *9* magnetic turning device for the supports *7*; *10* glass target held in supports *7*; *11* Al-sheet discharge electrode; *12* cold-trap, cooled by liquid air; *13* pumping line. By exchanging the electrode *11* for one of sputterable metal, the unit can be used for cathodic sputtering

In most cases today, one is not advised to make such equipment oneself. A series of evaporation plants are available from various manufacturers; they are very well constructed and are available both for universal requirements and for specialist mass-production purposes. Figures B 10-207 to B 10-212 show some of these plants, which usually come complete with vacuum system and control panel. Oil rotary and oil diffusion pumps are the rule. Larger equipment is provided with a high-capacity forepump for rapid pump-down of the evaporation chamber in the first stage of the process, and a similar type of pump of lower throughput which, after rough pumping is over, main-
[10.4] tains the backing vacuum for the diffusion pump (Fig. B 10-210A). The vacuum is usually measured with a PIRANI or PENNING gauge. Recently, fully-automatic mass-production equipment (Fig. B 10-123) has been built, with a turntable and 16 evapora-

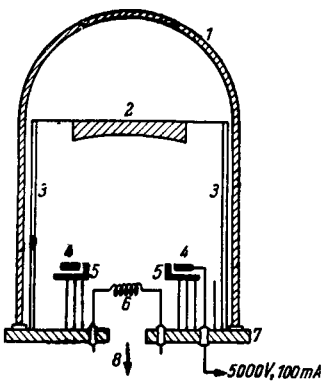


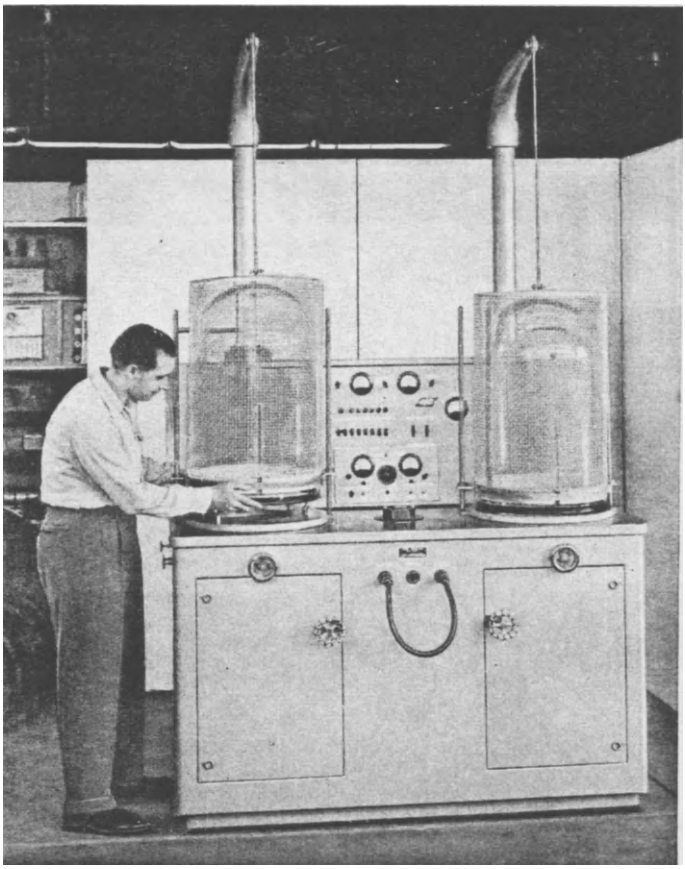
Fig. B 10-206 BENSON's design of evaporator

1 glass bell-jar; *2* glass target disk; *3* grounded metal cylinder; *4* annular discharge electrode; *5* grounded radiation screen; *6* vapor source; *7* grounded metal baseplate; *8* pumping connexion

tion chambers (dia. = 350 mm, height *ca.* 450 mm), capable of 20–120 runs/hr, according to load. Each chamber has its own oil diffusion pump, but the roughing pumps and automatic vacuum valves are common. One operator is enough for this plant, and he only has to unload and re-load the chambers with targets and when necessary, evaporant. There are cases where large numbers of big objects have to be coated, for instance TV tubes, whose fluorescent screens have to be metalized on the rear side with an Al film evaporated in HV; cf. 15.5.V. Use is made here of so-called "in-line exhaust systems", a recent development fully described in 10.5 (see also Fig. B 15-58).

Extreme cleanliness of the target is necessary to produce adherent evaporated layers on glass and other substrates, just as in sputtering. The procedures for cleaning glass recommended in 10.4.I, are applicable; chemical cleaning, especially by chromic sulfuric acid, brushing with ionized Bunsen flames ([2]STRONG), or with a corona discharge from a spark generator. The most efficient, however, has proved to be glow-discharge cleaning of the target surface ([1,3]STRONG, BENSON, KARASEV). Most modern commercial plant provides special Al electrodes for this (see, e.g., Fig. B 10-204, *9*, or Figs. B 10-205, *11*; B 10-208, *4*; B 10-210, *10*). Before HV has been reached in the chamber, when the residual air is at 10^{-1} to 10^{-2} Torr, a glow discharge is struck between the discharge electrode (or in the absence of one, the unheated heater wire of the vapor source) and the glass plate holder and the metal bell-jar; 2–5 kV D.C. is

applied to strike it, and it is held for 5–10 min. This treatment efficiently removes the adsorbed grease, gas and water vapor layers which impair the adherence of evaporated deposits. Apparently, Al discharge electrodes experience a slight sputtering effect which



[10.4]

Fig. B 10-207 Twin commercial evaporation plant with glass bell-jars (45 cm dia.) and guard cages, complete with pumps and control panel (made by CONSOLIDATED VACUUM CORP., Rochester, N.Y., USA)

deposits Al on the glass, Al_2O_3 is formed and the adherence is improved. For best adherence of the deposit the glow discharge is carried out as intensely as the thermal limitations of the glass allow ([1]HIESINGER). Where other target materials are involved, such as mica, paper, or plastics, the intensity of discharge is limited by decomposition of the substrate. Metal substrates must be connected to the negative side of the D.C. supply. Formation of uniform layers on metal targets requires them to be well degassed initially and then adequately cooled.

For cleaning the target, many workers recommend evacuation to diffusion pump pressure and then a special auxiliary gas filling of Ar (ANGERER), or of 10^{-3} to 10^{-4} Torr

of O_2 or H_2, followed by a 10 minutes glow discharge at 2–5 kV, 10–100 mA, with three or four intermediate flushings with O_2 ([3]STRONG). Addition of auxiliary gas at suitable pressure can help to produce an adequately prolonged and stable glow discharge if fed through a needle-valve under continuous (possibly throttled) pumping. However, air is the preferred gas for discharge cleaning of glass ([2]L. HOLLAND). Instead of discharge cleaning, the glass can be exposed under HV conditions to electron bombardment from a hot W cathode, the support being connected to a positive voltage. The glass surface

[10.4]

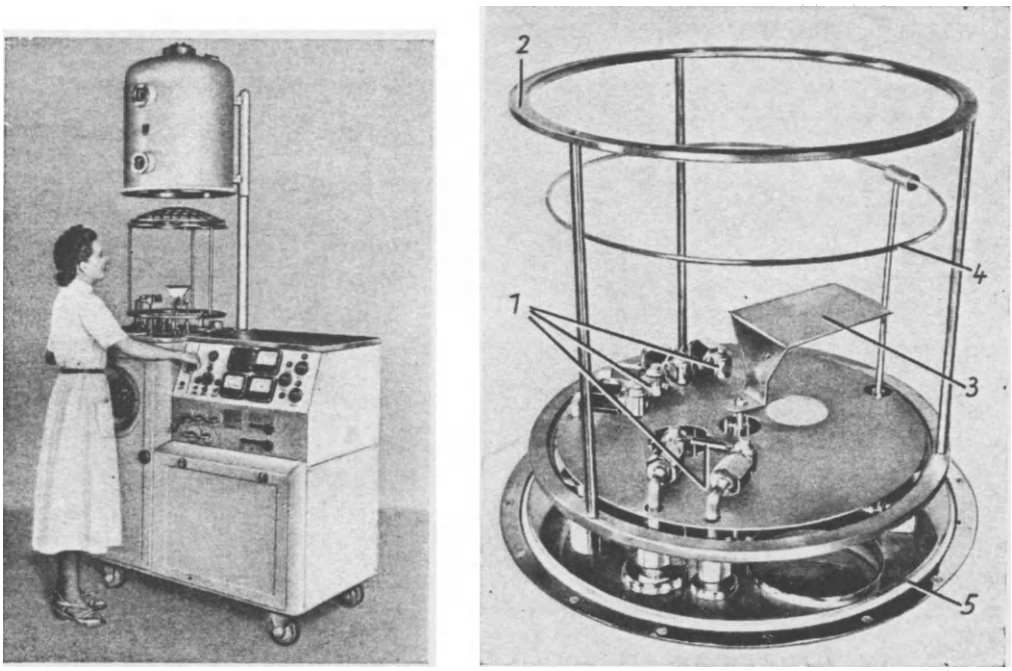


Fig. B 10-208 Commercial evaporator with stainless steel bell-jar (500 mm dia.) and hydraulic lift (made by GERÄTEBAUANSTALT BALZERS, Liechtenstein, type AB 500)

Above: overall view with control and measurement desk and complete pumping unit. *Below:* internal arrangement: *1* three separate vapor sources (D.H. boats, heater leads for 400 A max.); *2* rotatable support for the work to be coated (the holder dome provided can be seen at the left of the upper photograph; *3* baffle which can be positioned over each source by turning on a shaft; *4* discharge electrode; *5* rubber gasket ring

is cleaned, without significant overall heating or use of auxiliary gas, in a *high vacuum* and evaporation can then proceed at once without having to pump off discharge gas (see, however, [7]HOLLAND).

After glow discharge cleaning, the apparatus is exhausted to a HV and then heated, crucible and evaporant are degassed by cautious heating below evaporation temperature; the evaporant may also be fused at this point. If possible, the source should be covered during this time with a movable baffle (Fig. B 10-205) to protect the target surface from any evaporated impurities (RIEDMÜLLER). In many cases, such as aluminizing TV tube fluorescent screens, it is recommended that the whole forming process for the source (degassing and melting) should be undertaken as a separate process in a special

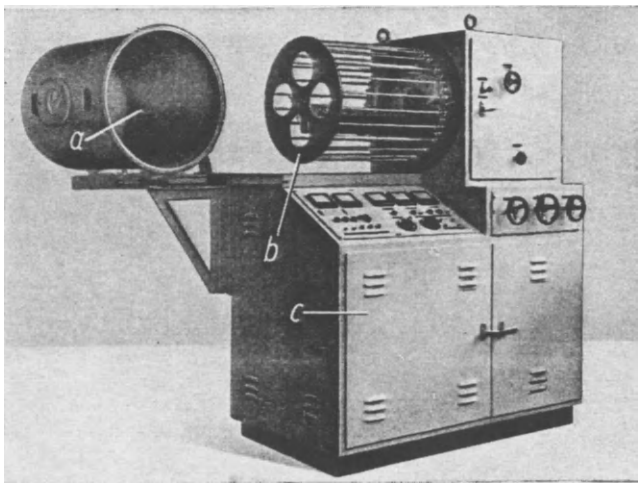


Fig. B 10-209 Commercial evaporation plant using D.H. strip boats as sources (made by A. PFEIFFER, Wetzlar)

a horizontally-pivoted vacuum jar of Al alloy (550 mm dia., 600 mm long); *b* rotating frame for targets; *c* complete pumping unit, discharge equipment, control and measurement desk

[10.4]

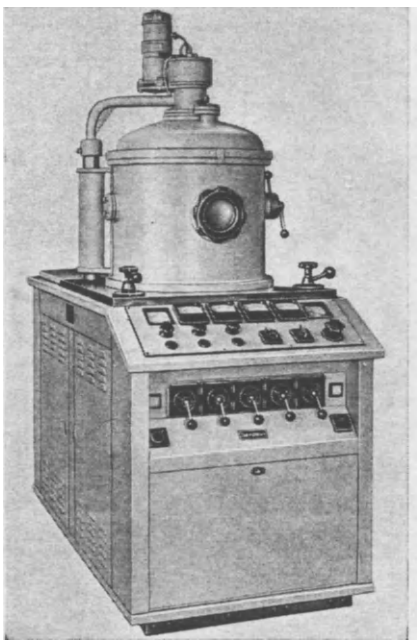


Fig. B 10-210 Commercial HV evaporation plant (courtesy of HERAEUS, Hanau)

Bell-jar dia. 620 mm, height 660 mm, pump-down time from 760 to 5×10^{-5} Torr, *ca.* 10 min. For design see Fig. B 10-210A

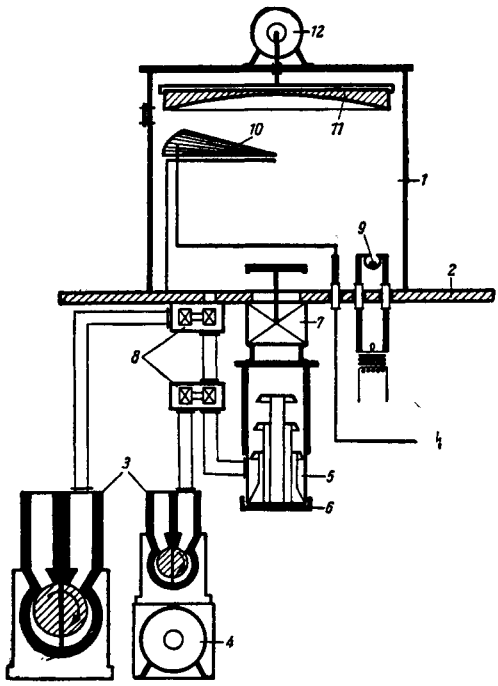


Fig. B 10-210A Design of Fig. B 10-210 equipment

1 vacuum chamber; *2* baseplate; *3* rotary fore-pumps; *4* drive motor; *5* diffusion pump; *6* heater for *5*; *7* main HV valve; *8* roughing valve; *9* vapor source; *10* glow discharge cathode; *11* glass target; *12* drive for turning *11*

auxiliary unit, an example of which is shown in Fig. B 10-214. This necessarily arises with metals which cannot easily be made to wet the heater in HV and thus have to be melted under H_2. An example is Cr.

The evaporation itself should not be started above 10^{-5} Torr if gas-free, bright and bubble-free deposits are to be achieved. Evaporation should be halted if outgassing raises the pressure above 5×10^{-5}.

[10.4]

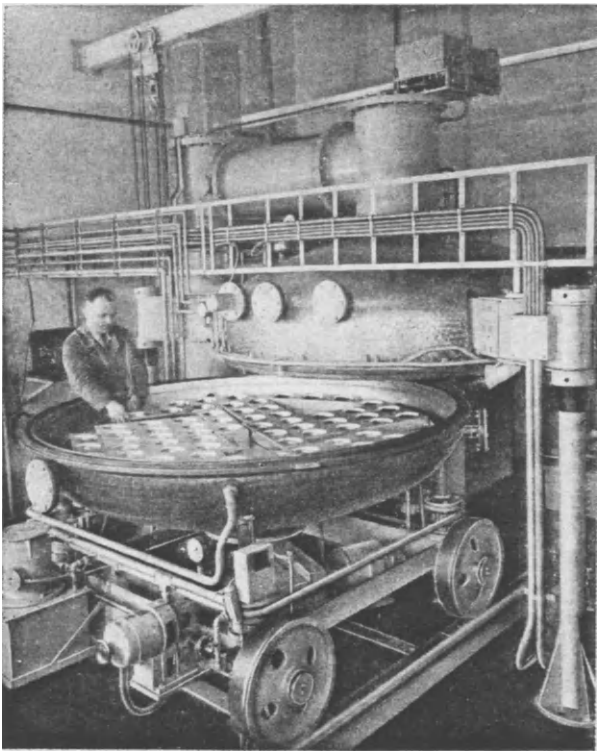


Fig. B 10-211 HV evaporator (type A 2000 V) for coating large numbers of articles (made by HERAEUS, Hanau, who also supplied the photograph)

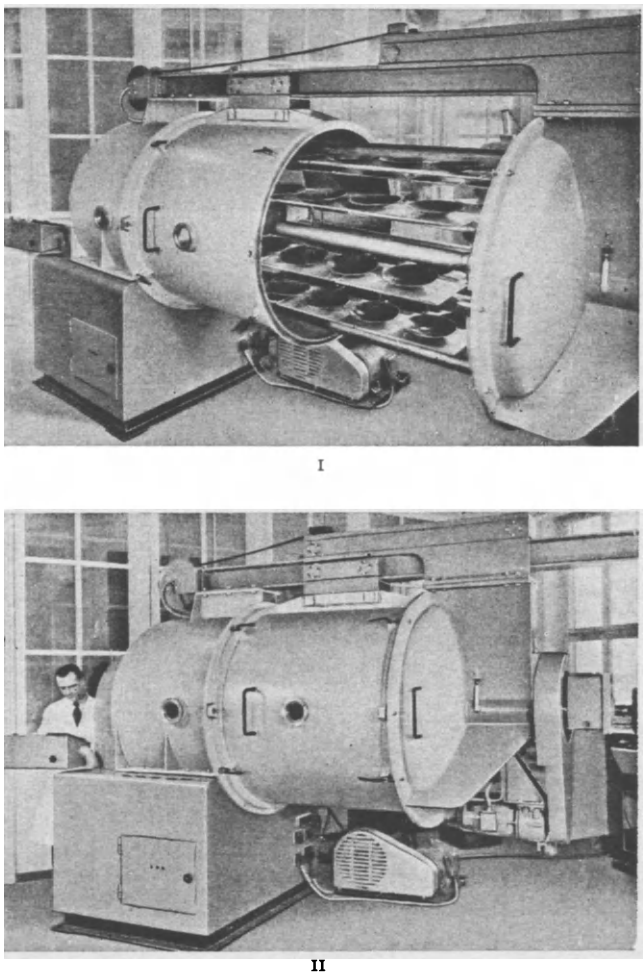
The apparatus consists of a top tank with evaporating devices, glow discharge electrode (cathode) and baffle plate, and a bottom tank with motor-driven turntable, and fixed to a lift-truck. The latter can be raised or lowered hydraulically. After lowering the truck lift and removing the truck, the top tank can be replenished with evaporant. Fore-pump capacity 180 cu. m/hr, diffusion pump speed 8000 liters/sec, pump-down time to 5×10^{-4} Torr, *ca.* 15 min (tank unloaded)

Liquid-air-cooled traps should be connected in series with any Hg-diffusion pump. Dry ice is not good enough, especially with Al evaporation because brown films will result; it is sufficient if oil pumps are employed. Above all, water and oil vapor should be excluded. The distance between hot source and target is normally 50–100 mm, but this must be raised to 300–600 mm if the target outgasses due to radiation of heat from the source. Large or round or irregular-shaped work must be rotated during the process, and it is often necessary to arrange several sources around the target. Since the stray deposits on the vessel walls occlude a good deal of gas as time goes on, and must be

removed, to save cleaning time the walls should be provided with special screens; these screens can be cleaned periodically in acid.

Table T 10–27 gives the evaporation temperatures needed for the individual evaporants. These are the values needed to raise the VP of the evaporant metal to 10^{-2} Torr

[10.4]



I

II

Fig. B 10-212 Large-capacity HV coating plant with horizontal chamber (made by GERÄTEBAUANSTALT BALZERS, Liechtenstein, type BA 1200)
(Dia. 1.2 m, length 2.3 m); I opened; II closed

(cf. also 9.5–4, vol. 1, pp. 882–889). The theoretical rate of evaporation for the given temperature is also included in the table, but naturally in practice it is not always reached because of suppressing effects. Finally, the last column of the table contains information, based on practical experience, for selection of the appropriate heater,

whose choice depends not only on temperature but more on certain properties like wettability by and chemical reactions with evaporant. These properties of the chief evaporants and heater materials are collected for clarity in Table T 10–28.

[10.4]

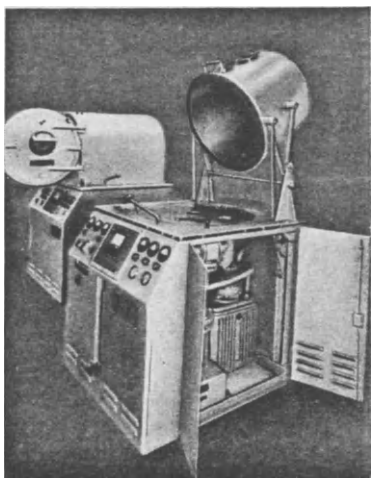


Fig. B 10-212A HV evaporation plants with vertical bell-jar and horizontal chamber, 630 mm dia. (made by DEUTSCHE VACUUMAPPARATE DREYER UND HOLLAND-MERTEN, Sangerhausen, GDR)

An *alloy* can only be evaporated directly if its components have the same VP at the evaporation temperature selected, as is sometimes the case with SnCu alloys ([1]HOLLAND), but is not so for brass (CuZn) where Zn comes off completely after a short time at 350°,

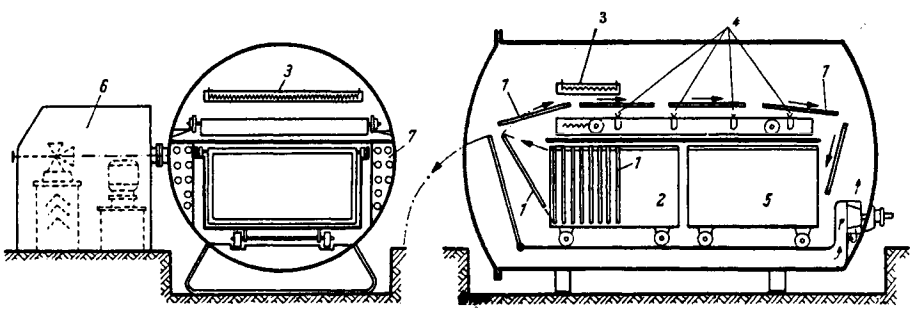
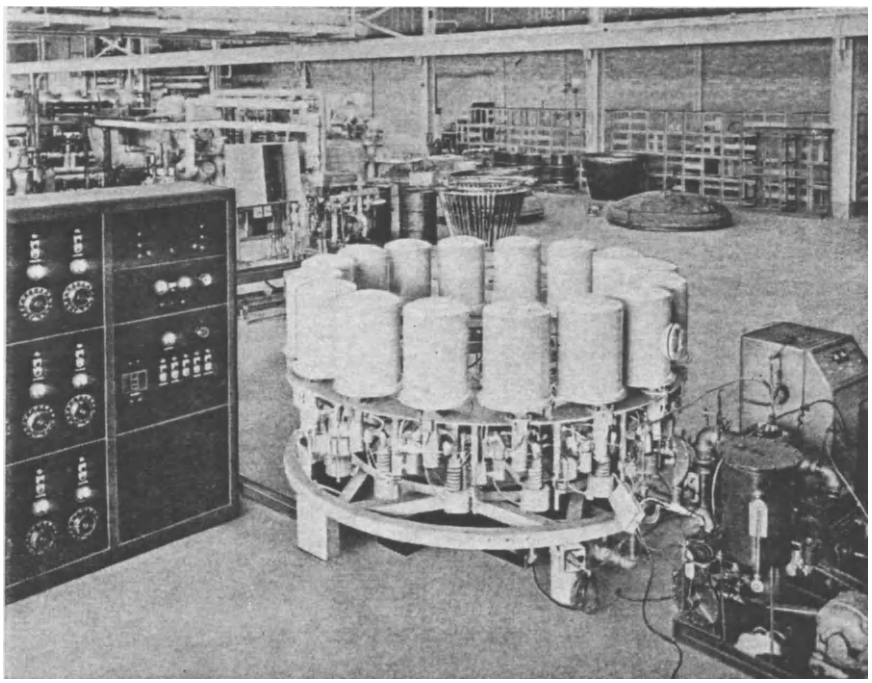


Fig. B 10-212B Plant for coating flat targets, e.g. rectifier plates or plate-shaped mounts (HOLLAND-MERTEN)

The targets (*1*), arranged vertically one behind the other in the lower section of the left-hand storage tank (*2*), are preheated by heater (*3*) and transported continuously in series over the sources (*4*) and returned to storage tank (*5*). The whole mechanism is retractable. (*6*) Diffusion pump station with control desk, (*7*) additional heating chamber

while Cu does not evaporate at the same rate below 1280°. The only possibility here is to evaporate from two separate sources at the same time but with heater temperatures set so that the evaporation rates of the alloy constituents correspond to the composition of the desired alloy deposit.

Alloys, and also refractory metals, can be evaporated as thin layers by the "exploding wire" technique, i.e. heavy current discharge from a capacitor, carried out in HV.



[10.4]

Fig. B 10-213 Fully-automatic plant for mass-production coating of small parts; plant has 16 metal vacuum chambers (350 mm dia., 450 mm high) on a turntable (made by CONSOLIDATED VACUUM CORP., Rochester, N.Y., USA)

By evaporation of metals in HV, deposits of 0.1–2 μ on glass can easily be made in a few minutes. Thicker layers are seldom needed and if occasion arises can be made by electroplating over the evaporated layer. Evaporated deposits above 20 μ thick tend

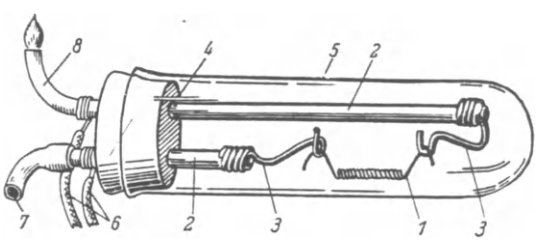


Fig. B 10-214 Auxiliary apparatus for making evaporation sources: fusing the evaporant metal on a heater coil in H_2 ([1]STRONG)

1 heater coil; *2* Cu tube current-lead, also acts as gas inlet and outlet; *3* support wires; *4* rubber bung; *5* glass tube; *6* current-leads; *7* gas line; *8* H_2 exit line (gas should be burnt at outlet for safety reasons)

to flake off as a rule. When depositing volatile metals (of low M.P.) adherence to glass can be increased by pre-depositing a molecular interlayer of a higher M.P. metal such as Ag or Cr (see also below for further details).

On smooth substrates like glass, specular highly reflecting layers are obtained, but on rough surfaces the deposit is diffusely reflecting. If matt objects are to be given a

TABLE T 10-27. PROPERTIES OF METALS AND SOME METAL COMPOUNDS RELATING TO HIGH VACUUM EVAPORATION ONTO GLASS AND SIMILAR MATERIALS

(ANGERER, BLEIWEIS, CALDWELL, COUNTRYMAN, [3]METHFESSEL, OLSEN)

[10.4]

METAL	M.P. (°C)	EVAPORATION TEMP. (°C)	EVAPORATION RATE $\left[\frac{10^{-5}\ g}{cm^2\ sec}\right]$	SUITABLE HEATER (IN ORDER OF DECREASING SUITABILITY)	FOOTNOTE NUMBER
Ag[1]	960.5	1047	17	Ta[2], Mo[2] [6] [26], Nb, Fe, W + Pt [3], W (silvered)[43], Chromel[4], Ni[5], BeO crucible	[8] [23] [49] [56]
Al[1]	658	996	8	W[7] [35] [39], Ta, Mo, Nb, Al_2O_3 crucible[36], ThO_2 crucible	[9] [10] [56]
As	(subl. 616)	280	22	Al_2O_3 crucible with W external heater wire	
Au[1]	1063	1465	20	W, Mo[26]	[11] [12] [22] [50]
B	2300	1365	5	W, graphite crucible	
Ba[1]	710	627	23	W, Ta, Mo, Nb, Fe, Ni, Chromel	[13] [44]
Be[1]	1280	1246	5	Ta, W[7], Mo, ThO_2 and BeO crucibles	[14]
Bi[1]	271	698	27	Chromel[4], Ta, W, Nb, Al_2O_3 and porcelain crucible (Ni crucible)	[44] [46]
C	≈3600	2680	4	Graphite crucible[15] or graphite sphere[16]	[57]
Ca	850	605	13	See Barium; also Al_2O_3 crucible	[17]
CaF_2	1392			W heater plated with Pt or Rh	[42]
Cd[1]	321	264[33]	27	Chromel[4], Nb, Ta, Fe, Al_2O_3 crucible, SiO_2 crucible (W[22])	[17] [44]
Ce	775	1305	17	W	
CeO_2				Thin W strip boat[59]	
Co[1]	1492	1649	10	Nb, Al_2O_3 or BeO, or graphite crucible[31]	[58]
Cr	1920	1205[33]	11	W[2] [12] [14] [17] [47], Cr[18], graphite crucible [15] [31]	[30] [48]
Cs	28	153	32	Porcelain and glass (micro) furnaces	
Cu[1]	1084	1273	12	Pt, W + Pt[3], Mo[19] [22] [26], Ta, Nb, Al_2O_3 crucible, graphite rods[20]	
Fe[1]	1535	1447[33]	10	W[7] [19], Fe[18] [34]; Al_2O_3 or BeO or SiO_2 crucible	
Ga	29.8	1093	13		
Ge[1]	958	1251	13	Ta, Mo, W, Al_2O_3 crucible	[44]
Hg	−38.8	48	46	Glass vessel, quartz apparatus	
In	156.4	952	18	W, Fe, Al_2O_3 crucible, Mo boat	[44]
Ir	2454	2560	15	Ir[16]	[23]
K	63.6	207	17	Glass vessels	
La	885	1381	17		
Li	185	514	5	Crucible of low-carbon steel + NiCr heater wire	
Mg[1]	657	443[33]	11	W, Ta, Mo, Nb, Fe, Ni, Chromel[4], Al_2O_3 crucible, Mg[18] [21]	[17] [44]
MgF_2	1221	>1221		Mo boat	[42]
Mn[1]	1244	980[23]	12	W[8], Mo, Ta, Nb, Mn[18], Al_2O_3 crucible, graphite crucible	
Mo	2622	2533	11	Mo[18], graphite crucible[15]	[39] possibly[23]
Na	97.7	291	12	Glass vessel, possibly enamelled with Na-resistant glass	
Na_3AlF_6	1100				[42]

TABLE T 10-27 *(continued)*

METAL	M.P. (°C)	EVAPORATION TEMP. (°C)	EVAPORATION RATE $\left[\frac{10^{-5}\ g}{cm^2\ sec}\right]$	SUITABLE HEATER (IN ORDER OF DECREASING SUITABILITY)	FOOTNOTE NUMBER
Nb[1]	1950	≈2700	≈10	Nb[15] [16], W[11]	
Ni[1]	1453	1510	11	W[7] [19], W[22] [17], Ni at 1420 °C[18] [34], Al_2O_3 or graphite crucible	(54)
Os	2700	2667	15		(23)
Pb[1]	327	718	27	Fe, Ni, Chromel[4], Al_2O_3 crucible, W[26], Mo boat	(44) (52) [10.4]
Pd	1555	1566	14	W[11]	
Pt[1]	1773	2090	17	W[11], W[19], W[22], graphite crucible [31], Pt at 1745 °C[18]	(23) (24) (55)
Rb	39	165	26	Porcelain or glass vessel	
Rh	1966	2150	12	Rh at 1930 °C[18], ThO_2 crucible (2150° to 2200 °C), graphite crucible[15], (W[22])	(25) (39) possibly (23)
Ru	2500	2430	11.3		
Sb[1]	630	678	30	Chromel[4], Ta, W, Al_2O_3 crucible (Ni crucible)	(44) (51)
Se[1]	217	234	26	Mo, Fe, W[26], Ni[26], Chromel[4], Al_2O_3 or BeO crucible, Mo or Ta boat	
Si	1414	1343	8	W + Pt[3], Ta[26], graphite crucible[29] [31], BeO crucible	(27) (28)
SiO		1100–1250		W[26], Ta[26], Mo[26], graphite crucible	(32) (45)
SiC				W[26], graphite crucible	
Sn[1]	232	1190	20	Chromel[4], Mo, Fe, Al_2O_3 crucible, (W[22])	(44) (53)
Sr[1]	771	549		W, Ta, Mo, Nb, Fe, Ni, Chromel[4]	(44) (12)
Ta	2996	3070	≈14	Ta[15] [16]	
Te[1]	452	≈670	≈25	W, Ta, Mo, Nb, Ni, Fe, Chromel[4], Al_2O_3 crucible	(37) (44)
Th[1]	1827	2196	18	Mo, W	(44)
Ti[1]	1727	1546		Ta, W, Ti[18], graphite crucible, TiC boat [60]	(40)
TiO_2					
Tl[1]	302.5	606	28	Ni, Fe, Nb, Ta, W, Al_2O_3 crucible	
U	1689	1898	19	W[44]	
V[1]	1720	1888	9	W, Mo[44], graphite crucible	
W	3382	3310	14	W[16], graphite crucible [15] [31]	(39)
Y	1475	1649	13		
Zn[1]	419.5	343[33]	19	W, Ta, Mo, Nb, Al_2O_3 crucible, (Fe[22])	
ZnS	[41]			Mo boat[41]	(42)
Zr	1860	2001	12	W[11], graphite crucible	(44)

Footnotes to Table T 10-27

[1] Cf. also Table T 10-28.

[2] One method: close-wound coil (wire dia. 0.8 mm, mandrel 3 mm, *ca.* 14 turns), in which the evaporant wire or chips (Fig. B 10-203, *e*) are inserted; better method: conical heater coil (Fig. B 10-203, *i* and *k*), since the evaporant adheres poorly to heater wire; see also footnote 19.

[3] First wind thin Pt wire on W, then overwind thicker wire of evaporant metal which will adhere to the Pt "grid" after melting.

[4] Chromel: 89–91 Ni; 4.7–9.8 Cr; 0.2–1.9 Mn; 0–1.4 Si; 0.9–1.01 Fe; 0–0.1 C.

[5] Deposit contains some Ni.

(6) Ag evaporant electroplated on Mo, from standard cyanide bath at low current density; silvered heater wires can be stored for several days under distilled water (HOWARD); cf. also footnote 43.

(7) Since there is a slight reaction with the evaporant metal, W wire dia. should be 0.7–1.0 mm, or the heater should be made of twisted W wires (3–4 wires, 0.5 mm dia. each). For heater coils it is best to use: 8 mm mandrel dia., 6 mm pitch.

(8) Attach as per Fig. B 10-203, *d*. Forming (melting) at 800°.

(9) See also GREENLAND, JIOA ¹STRONG. A chrome strike improves the adherence of Al deposits provided both layers are evaporated in succession from two separate heaters without letting down to air.

(10) Table T 10–29 contains a complete industrial process for making inner reflectors of Al for floodlights and IR lamps (see also Fig. B 10-217).

[10.4]

(11) Coil evaporant wire on heater wire as per Fig. B 10-203, *f*; possibly melt in H_2 or He (see also Fig. B 4.1-8, Vol. 1).

(12) Close-wound cone as per Fig. B 10-203, *i*, made of 3 W strands of 0.5 mm dia.

(13) See Chapter 27 (Flash getters) for evaporation by H.F. heating from filled Fe or Ni tubes.

(14) Forming in auxiliary apparatus (Fig. B 10-214) in H_2.

(15) Heated by electron bombardment (Fig. B 10-203, *u*).

(16) Heated in focal spot of an X-ray tube cathode (Fig. B 10-203, *v*).

(17) Form and degas in He in auxiliary apparatus (Fig. B 10-214).

(18) Heated by direct current passage in form of wire or strip as per Fig. B 10-202 (Sublimation).

(19) Heater made of 4 twisted strands each 0.5 mm dia., of which one is the evaporant.

(20) Directly heated and provided with drilled hole in which evaporant is placed (see, e.g., Fig. B 10-203, *t*).

(21) See Chapter 27 (Flash getters) for evaporation by H.F. after welding to metal flag.

(22) Evaporant electroplated on W.

(23) Better to sputter if making external mirrors or metalizing glass plates (see 10.4.IV, esp. Table T 10–26).

(24) Heat very slowly otherwise small balls fly off, or the deposit will be gray.

(25) For commercial Rh mirrors, see GREENLAND, JIOA, for example.

(26) D.H. boat made from strip as per Fig. B 10-203, *m*, *n*, *o*, o_1, o_2.

(27) Before Si evap., first shut off vapor source with baffle and drive off SiO_2 and SiO.

(28) When evaporating from ThO_2 or Al_2O_3 crucible, Si comes off as SiO (silicon monoxide).

(29) Also can be done with a graphite rod, 5 mm dia., 50 mm long, drilled to take evaporant and heated to 2200° by direct current passage (Fig. B 10-203, *t*).

(30) Blank off the source as much as possible when evaporation is in initial stages.

(31) Metal carbides form which do not come over but can reduce the rate of evaporation, and necessitate frequent replacement of graphite crucible.

(32) See, e.g., HASS, Fig. B 10-215.

(33) Sublimation.

(34) Also by H.F. heating.

(35) After loading the coil with Al riders (as per Fig. B 10-203, *d*), it is recommended that the W heater + Al be flamed with a gas flame to clean off grease. Then position in bell-jar and pump out.

(36) Also conical heater coil (max. dia. 6 mm, height 6 mm) as in Fig. B 10-203, *i*, made of Al_2O_3-coated W wire of 0.5 mm dia., with conical crucible insert, made of Ta sheet 0.25 mm thick (KELLY).

(37) Te adheres well to glass.

(38) Recently, ThW has been recommended instead of pure W.

(39) Very hard to evaporate, only thin layers after prolonged evaporation.

(40) Pure layers require vacua better than 10^{-5} Torr or TiO–TiN films are produced which have little optical value.

(41) Sublimed from the solid phase (subl. point *ca.* 1180° at 760 Torr). It is recommended that powdered ZnS be compacted to 2–3 mm thick disks which are vacuum-degassed, slightly sintered and then put in box-shaped Mo boats. Material prepared in this way does not tend to spatter as powder does (ROSS).

(42) See text 10.4.VII.

(43) Etch W wire as cathode in H_2SO_4 with Pt anode, then at once silver-plate in cyanide bath (25 g calcium cyanide, 15 g silver nitrate, 1 liter distilled water) with Ag anode. Load silvered W wire with U-shaped riders 10 mm long, made from flattened Ag wire, 0.5 mm dia. (see Fig. B 10-203, *d*, and ROIG).

(44) D.H. wire heaters coiled as spiral as per Fig. B 10-203, *i* or *k*.
(45) Cf. Fig. B 11-5B.
(46) Bi layers have a light reddish tint.
(47) MORAVEC recommends electroplating the W heater with evaporant and forming as per footnote 17.
(48) Evaporated Cr layers are usually very thin and are not bright (SEITER).
(49) Ag layers not so resistant as Al.
(50) Au deposits tend to surface diffusion so that Au also appears on the rear of the target.
(51) Sb layers are highly reflecting but show a grayish tinge.
(52) In air, Pb layers rapidly turn gray and diffuse-reflecting.
(53) Sn layers are perfectly white.
(54) Ni deposits are less lustrous than Cr. [10.4]
(55) Pt layers have a brilliant lustre.
(56) Continuous evap. by D.H. crucible made of graphite + C addition, or TiC, or TaC (REICHELT).
(57) Also with 2 pointed C electrodes which give a high-resistance contact when their points are pressed together (BRADLEY).
(58) Pure oxide crucible with embedded W spiral, since the metal reacts strongly with W, Ta, Mo, or Nb to form alloys.
(59) Powdered CeO_2 first pressed to thin plates, pre-sintered and pre-degassed in HV.
(60) Evap. from TiO in an O_2 atmosphere of $7–10 \times 10^{-5}$ Torr (ROSS); cf. also Swiss Patent 322265.

highly reflecting metalized surface, they should be first coated with a smooth lacquer, preferably one which outgasses as little as possible in HV and has a low VP. For example, simple reflectors for electric flashlights or lanterns are made from ordinary hot-galvanized sheet iron, and after dry-air blasting, are sprayed on the mirror side with a black smooth japan lacquer which is then oven-dried. The reflectors are placed in cage-like holders and arranged in large numbers round the vapor source which coats them with at least 10^{-5} cm of Al. This produces in a few minutes very durable high reflectivity mirrors of silvery appearance.

Semi-transparent layers can also be deposited by HV evaporation, of thickness about 10^{-6} cm. The rate of evaporation is kept purposely low and the transmission can be continuously monitored by light-beam and photocells during the process (Fig. B 10-223). This is the process by which the reflexion and transmission curves of Fig. B 10-214A were measured.

The metallic deposits are crystalline and when glass is the substrate each plane of crystals of the deposit is parallel to the plane of the surface of condensation. With metal substrates, the structure of the metal deposit depends strongly on the type and temperature of the target; the structure of the evaporated layer generally assumes, more or less, the crystal orientation of the substrate. This is particularly the case with low-melting metals which form relatively large crystals when deposited, while the evaporated layers of refractory metals have a microcrystalline structure (LEVINSTEIN).

Protective layers. A special problem with deposited layers, even sputtered ones, is protection against corrosion. The problem is most acute with mirrors exposed to the continuous effects of ordinary atmosphere and which must still retain their reflectivity unaltered for as long as possible.

High-melting metal deposits on refractory substrates such as quartz can be coated with a thin layer of SiO_2; the metalized object is placed in a space roughed out with a forepump and exposed to ethyl silicate vapor at the same time being heated to 850°

TABLE T 10–28. DEGREE OF WETTING (*b*), EASE OF EVAPORATION (*v*), AND DEGREE OF REACTION (*r*) OF EVAPORANT METAL WITH VARIOUS HEATER MATERIALS (CALDWELL); NUMERICAL RATING[1]

HEATER / METAL	Ag	Chromel	Fe	Mo	Nb	Ni	Pt	Ta	W
	b/v/r	b/v/r	b/v/r	b/v/r	b/v/r	b/v/r	b/v/r	b/v/r	b/v/r
Ag	—	1/1/1	1/1/1	1/1/1	1/1/1	1/1/1	—	1/1/1	1/1/1
Al	1/3/3	1/3/3	1/3/3	1/1/2	1/1/2	1/1/2	—	1/1/2	1/1/2
Au	—	1/3/2	1/3/2	2/1/1	1/2/2	1/3/2	—	1/2/2	2/1/1
[10.4] Ba	1/1/1	1/1/1	1/1/1	1/1/1	1/1/1	1/1/1	—	1/1/1	1/1/1
Be	—	3/3/1	3/2/1	1/1/2	3/2/1	1/3/3	—	1/1/1	1/1/2
Bi	2/3/3	1/1/1	3/[2]/1	2/1/1	2/1/1	1/3/1	—	2/1/1	2/1/1
Cd	3/2/1	1/1/1	2/1/1	3/3/1	1/1/1	3/3/1	—	3/[2]/1	3/3/1
Co	—	—	—	2/3/3	2/2/3	—	1/3/3	3/3/3	3/3/3
Cu	—	1/1/3	1/1/3	2/1/1	2/1/1	1/2/3	—	2/1/1	3/3/1
Fe	—	—	—	1/3/3	1/3/2	—	1/3/3	3/3/3	1/[3]/2
Ge	—	—	—	1/1/1	—	—	—	1/1/1	—
Mg	—	3/1/1	3/1/1	3/1/1	3/1/1	3/1/1	—	3/1/1	3/1/1
Mn	—	1/2/[4]	3/2/[4]	1/1/1	1/1/1	1/3/[4]	—	1/1/1	1/1/1
Nb	—	—	—	3/3/1	—	—	—	3/3/1	3/3/3
Ni	—	—	—	1/3/3	1/3/3	—	1/3/3	1/3/3	1/[3]/3
Pb	1/3/3	1/1/1	1/1/1	3/[2]/1	3/[2]/1	1/1/1	—	3/[2]/1	3/3/1
Pt	—	—	—	1/3/3	1/3/3	—	—	1/3/3	1/[5]/2
Sb	2/3/3	1/1/1	2/3/3	3/3/1	3/3/1	1/3/1	—	2/2/1	3/[2]/1
Se	1/1/2	1/1/1	1/1/1	1/1/1	1/1/1	2/1/1	—	3/[2]/1	3/[2]/1
Sn	3/[2]/3	1/1/1	2/1/1	2/1/1	3/[2]/1	3/3/1	—	2/1/1	3/3/1
Sr	3/3/1	1/1/1	1/1/1	1/1/1	1/1/1	[6]/1/1	—	[6]/1/1	1/1/1
Te	1/3/3	1/1/1	1/1/1	1/1/1	1/1/1	1/1/1	—	1/1/1	1/1/1
Th	—	—	—	3/1/1	—	—	—	3/3/1	1/2/1
Ti	—	—	—	1/2/3	1/2/1	—	—	1/1/1	1/1/3
Tl	1/3/3	3/[2]/1	1/1/1	3/[2]/1	1/1/1	1/1/1	—	2/1/1	2/1/1
V	—	—	—	1/1/1	1/2/1	—	—	1/3/3	1/1/2
Zn	1/3/2	1/3/3	1/3/3	1/1/1	1/1/1	1/3/3	—	1/1/1	1/1/1

[1] Key to abbreviations: b 1 wets well
b 2 adequate wetting
b 3 does not wet
r 1 no reaction between heater wire and metal
r 2 small reaction between heater and metal
r 3 intense reaction; heater burn-out
v 1 easily evaporates
v 2 slow evaporation
v 3 no evaporation

[2] Evaporant occasionally drops from heater.

[3] Forms low-melting alloys. Evaporation possible if thick heaters used.

[4] Heater readily burns out.

[5] Pt evaporates very slowly.

[6] Wetting poor because high-melting Sr compound is formed which separates metal from heater.

(LAW). The ethyl silicate vapor is decomposed at this temperature and the target becomes coated with SiO_2 at 0.03 μ/min of cracking time at 850°. The coat is harder the higher the target temperature, but 900° should not be exceeded or crystal growth takes place.

The VP of ethyl silicate at room temperature is 1.8 Torr. A cold trap should be provided to keep the vapor from the pump. Liquid ethyl silicate is held in a calibrated side tube attached to the apparatus and is evaporated into the reaction volume via a trap at 0.1 cm^3/min.

Vacuum-evaporated layers of Al on glass, etc., cannot withstand such high temperatures; they can be given very effective protection by direct evaporation of SiO_2 in HV. If one simply places a small rod of silica glass 1 mm dia. in a close-fitting coil of 0.5 mm W wire, the silica is easily evaporated but the film is slightly discolored due to the pres- [10.4]

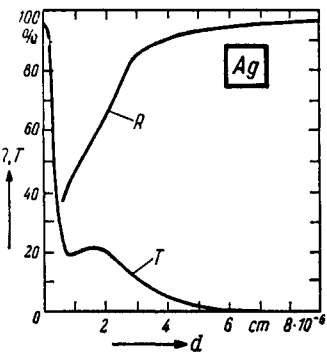


Fig. B 10-214A Reflexion R and transmission T of Ag layers deposited on glass, measured as per Fig. B 10-223, with monochromatic (5780 Å) light. R and T as functions of layer thickness d (DUFOUR)

ence of brown tungsten oxide. Pure quartz deposits are obtained by electron bombardment heating of a Ta crucible filled with fused quartz. In recent quartz coating processes ([1]HIESINGER, NAT. RES. CORP.), the starting material is not SiO_2 but SiO, which can be evaporated at 1100–1250° in HV, and more easily than SiO_2 (cf. Fig. B 11-5B); the deposit is then fully converted to SiO_2 in air. Figure B 10-215 shows an example of apparatus in which Al and then SiO can be evaporated in the same vacuum.

Pure SiO can now be obtained commercially at a reasonable price from such firms as HERAEUS, Hanau, and the NATIONAL RESEARCH CORP., Cambridge, 42, Mass. One can make SiO (GREENLAND, [1]HASS) by first grinding pure quartz very fine in a ball-mill, and then removing any coarse particles by sedimentation. The powder is thoroughly hot-dried and mixed with fine Si powder in the stochiometric ratio of 1 Si + 2 SiO_2. The mix is put in the end of a horizontal silica tube sealed at one end and at the other projecting from an electrical furnace; the mix is heated under the best possible vacuum to over 1300°. Brownish-black SiO condenses on the cold walls of the quartz tube and can be used without further treatment for evaporating on mirrors. According to GRUBE, one can also proceed as in Fig. B 10-214B; a definite temperature gradient is maintained along a tubular reaction vessel and two separate Ni cylinders are arranged behind the reaction mix. During the approximately 4 hours of heating, clearly distinguishable condensates form in the two spatially separated Ni tubes; a brownish (possibly also

yellowish and tacky) mass of crystalline Si and amorphous SiO_2, and in the Ni tube in the cooler zone, a glassy black-brown condensate of SiO with at most 4% SiO_2. Any SiO not immediately used should be stored dry in evacuated containers or under oxygen-free protective gases.

Recently, vacuum-evaporated layers of SiO, which are amorphous, have become important as supports (backings) for electron diffraction measurements and as a preparatory agent in electron metallography ([2]HASS, SCHULZE).

[10.4]

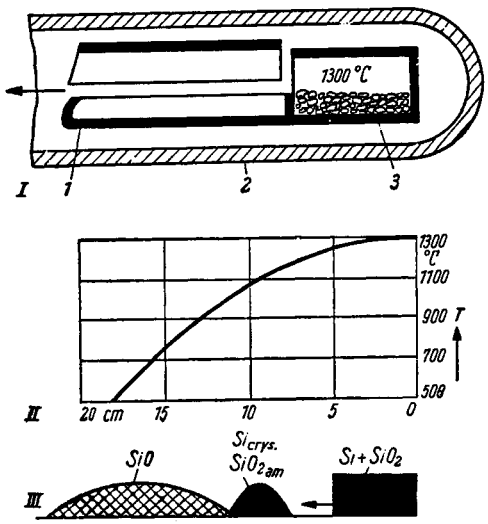


Fig. B 10-214B Production of pure SiO in HV by reduction of fine SiO_2 powder by fine Si powder (GRUBE)

I design of the apparatus: *1* boat with convex cover; *2* quartz glass or alumina tube, evacuated to and held at 0.1 Torr or below by oil diffusion pump; *3* reaction mix. II temperature gradient along evacuated tube. III distribution of condensate after reaction

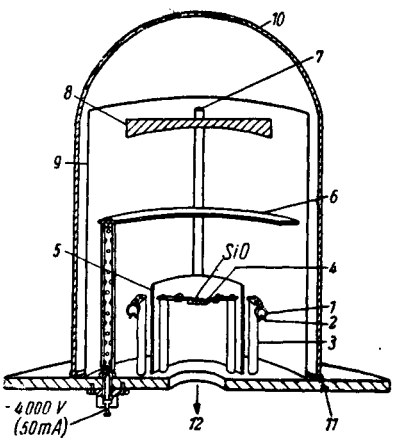


Fig. B 10-215 Apparatus for evaporating Al layers, immediately followed by evaporation of SiO protective layer (HASS)

1 W coil; *2* Al riders; *3* heater lead; *4* D.H. W, Ta or Mo boat (see also Fig. B 10-203, *m*), filled with SiO; *5* radiation shield cylinder; *6* discharge electrode; *7* mirror support; *8* glass target; *9* hard-glass cylinder to prevent coating of glass wall; *10* glass bell-jar; *11* metal baseplate; *12* to pump

Many manufacturers recommend that for complete conversion to SiO_2 the evaporated SiO layers be held for several hours at 500°. Optimal reflectivities of quartz-coated Al mirrors (85.5–90%) in the visible occur for protective layer thicknesses of 2250 Å (2.25×10^{-5} cm), and the mirror has a bluish tint. Reflexion peaks occur for SiO_2 thicknesses of $0.45\,\lambda$, where λ is the average wavelength of the reflected radiation. Such protective layers improve corrosion resistance to tropical and marine conditions; SiO-coated Al films can withstand an hour in 10% NaOH and prolonged heating up to 450° with practically no change in reflectance. Besides this, the wiping resistance and scratch hardness are improved. Compared with unprotected layers, the abrasion resistance is increased by a hundred-fold. SiO protective layers are suitable for all metals which form refractory oxide layers in air, such as Cr and Cu films; this is not the case with noble

metals which do not form a strong bond with the protective coating, and thus there is a tendency for flaking of the SiO.

Ag layers are well known for discoloration in air because of their sensitivity to S. They can be protected by a thin evaporated layer of Al, which is then completely oxidized to Al_2O_3 in air. The Al thickness required is about $^1/_{16}$ of a half-mirror of Al. Such a film can therefore be made very precisely as follows; a glass plate is placed near the source without shadowing the target at about quarter the distance between source

[10.4]

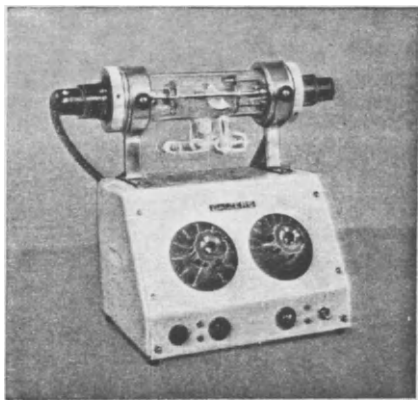


Fig. B 10-215A Small laboratory shadow-casting unit for oblique (20–90°) coating of microscope specimens with metal (made by BALZERS, Liechtenstein)

Total time per shadowing operation ca. 10 min

and target, and the evaporation of Al is stopped as soon as the monitoring plate has acquired a half-mirror as tested by photocell and light source as per Fig. B 10-223 ([1]STRONG). There are other protective layers for Ag films, such as fluorides of Ca or Mg. It has been discovered in recent investigations that high corrosion resistance of Ag layers can be achieved by evaporating a thorium tetrafluoride film and converting this to the oxide ([1]HIESINGER). These coatings have a low refractive index and do not absorb in the visible or UV ranges (ROSS).

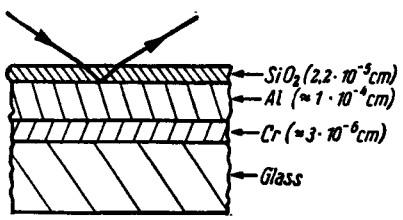


Fig. B 10-215B Construction of vacuum-evaporated Al mirror for highest-grade optical work (made by EVAPORATED METAL FILMS CORP., Ithaca, N.Y., USA)

Technical applications of the vacuum evaporation process. Metalization of glass, especially flats, of quartz oscillator crystals, mica, ceramics and other inorganic materials. In the case of quartz crystals, the electrode thicknesses are for Ag 0.6–1.5 μ = 0.6–1.5 mg/cm², for Au 0.25 μ = 0.5 mg/cm² approx., and for Al 0.6 μ = 0.16 mg/cm². See AWENDER for apparatus to metalize quartz crystals, which are first excited and then adjusted to desired frequency by depositing a precise amount of metal. See the note at the end of 10.4.V, on metalization of organic materials by vacuum evaporation. The process is also used for coating optical glass with mechanically resistant layers,

TABLE T 10–29. COMPLETE MANUFACTURING SCHEDULE FOR INTERNAL REFLECTORS MADE BY EVAPORATION OF ALUMINIUM, AS USED FOR AIRPLANE LANDING LAMPS, INFRA-RED LAMPS AND SIMILAR DEVICES (ROSE)

A. Glass cleaning:

1. Wash glass with hot water.
2. Wash glass with hot alkaline reagent.
3. As 1.
4. Wash with HF (3–15%); weak acid etches the surface invisibly and improves the adherence of the metal film, and concentrated acid is used to produce slight internal frosting of the "window" in the Al layer.

[10.4]

5. As 1.
6. Rinse in hot distilled water.
7. Hot-air dry the glass.

B. Metalization process[1]:

1. Drying: as per A 7, to remove any moisture that may have condensed in the tubes during storage.
2. Heater loading: load W coil source heater with Al riders (see Fig. B 10-203, *d*) or with folded foil as per Fig. B 10-216. Al better than 99% pure. Weight of Al to suit extent of target to be metalized, e.g. for lamps of average size, 0.3 g.
3. Mounting: placing of glass parts in aluminizing rig;
   (a) small parts in frame support, then arrange frame to surround source, and under bell-jar which is sealed with rubber gasket;
   (b) large glass reflectors (e.g. for projection lamps, see Fig. B 10-161A) dropped over sources as per Fig. B 10-216 and then cover whole assembly with bell-jar.
   (c) narrow-necked sealed-off tubes (IR lamps, TV tubes, etc.): replace the bell-jar and the neck is sealed vacuum-tight with a fitting neoprene bung (see Fig. B 10-217), through which pass the pumping line and leads to the heater to make vacuum-tight seals. The source itself is mounted on the ends of the leads at a height depending on the size of the envelope.
4. Pumping: place implosion guard (plastic material) over each bell-jar or over each tube. Exhaust with oil diffusion pump to 10^{-4} to 5×10^{-5} Torr; use liquid air trap with Hg diffusion pump.
5. Forming the vapor source: pre-heat Al riders for 10 sec in W coil without melting; then raise current till riders melt.
6. Flashing: raise heater current further till Al evaporates rapidly, not allowing vacuum to deteriorate to 10^{-4} Torr or above at any time.
7. Setting: let in dry air, raise bell-jar, dismantle reflector assembly (see Fig. B 10-218) or in the case of narrow-necked tubes (Fig. B 10-217) pull tube off bung. Then heat the mirror(s) in air with IR lamps for 3–5 min to form thin Al_2O_3 film (any IR source will serve for this).[2]

C. Making the window:

1. *Etching:* if a transparent window is required at the front of the lamp bulb, the film is removed at this region by etching away the Al[3]. A dilute solution of NaOH with small addition of alcohol[4] is poured into the tube which stands upright in a rack, and the part of the Al film wetted by the solution is dissolved in 2–3 min. The etching solution is introduced and sucked out through a tube so the solution only contacts the area of film that is to be etched off. The lamp remains fixed in the frame for the whole operation. Reflectors of the type in Fig. B 10-218 are dipped into the solution far enough to take off the Al coat in the region of the sealing edge.
2. *Removal of residual etching reagent:* hot water is pumped in to remove the last drops of solution. The tubes are removed from the rack and rinsed off in hot water[5].
3. *Spray cleaning:* neck of tube inserted in a fountain. Thorough washing of inner surface[5].
4. *Dry:* with hot air.
5. *Inspect.*

for applying protective and insulating layers to metal ("Surface Finishing", see, e.g., REICHELT), making carrier or support films and shadow-casting on samples for electron microscopy (Fig. B 10-215A); here Au, Cr, Pt, Pd and other metals are evaporated at an oblique angle of 10–40°; details of the process are given by WYCKOFF, for example.

Compared with cathodic sputtering, vacuum evaporation produces very gas-free deposits, and is distinguished by relative rapidity and simplicity; also, internal coatings can be applied to precisely predetermined areas of vessels or envelopes.

Windows can be made in metal deposits inside tubes by masking or by coating the appropriate part of the glass envelope with a mica sheet or glass balls, removed after deposition is complete, or in the case of sealed-off tubes, tipped into the base of the tube; another way is partly to etch away the metal deposit (example in part C of Table T 10–29). [10.4]

Regarding the application of specific metal evaporants, the following remarks should be made:

Ag: very pure evaporated layers withstand S vapors like H_2S and also O_3 without tarnishing, whereas Ag layers made by wet chemical processes (see 10.4.III) are attacked. However, rubber containing S will attack the film locally, if in direct contact. Ag evaporated films strengthen with aging and this process can be accelerated and the effect increased by the influence of H_2O_2 vapor (ANGERER). Like other noble metal layers, Ag films can be more easily made by cathodic sputtering if the target surface is an external one. Ag is often used for making metal deposits on mica plates of capacitors, which can then be soft-soldered. It is also often used for internal coating of photocells as a substrate for the light-sensitive alkali layer. For optical mirrors, the application of Ag has been largely shelved in favor of Al.

Al: this is the most important *evaporant* metal, especially as it virtually cannot be sputtered. Pure, bright Al layers made by vacuum evaporation have almost the same reflectance as Ag in the visible, but the UV reflectance is higher by far.

These properties are retained without a special protective coating because of the thin and optically harmless Al_2O_3 film which forms in air and makes the Al layer more corrosion-resistant than Ag. This corrosion-resistance can also be relatively easily improved by quartz-coating, in contrast to Ag; the surface hardness is also improved. The adherence of Al to glass is greater than that of Ag, and can be still further increased by a thin interlayer of evaporated Cr, provided this is applied by the aid of a separate source directly before aluminizing without letting down to air. Figure B 10-215B shows the cross-section of a modern Al mirror for the highest-grade optical

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(Footnotes to Table T 10–29)

(1) Large numbers would be processed automatically.

(2) This film is shown by experience to be less sensitive to later oxidation and produces sharp edges when the window is etched in the Al layer as per C 1.

(3) The window can in certain cases be covered with a mica or metal disk or with glass balls to eliminate the need for subsequent etching of the Al layer.

(4) To reduce the surface tension of the solution and hence improve wetting of the Al film by the solution.

(5) Open reflectors of the type in Fig. B 10-218 are treated analogously.

[10.4]

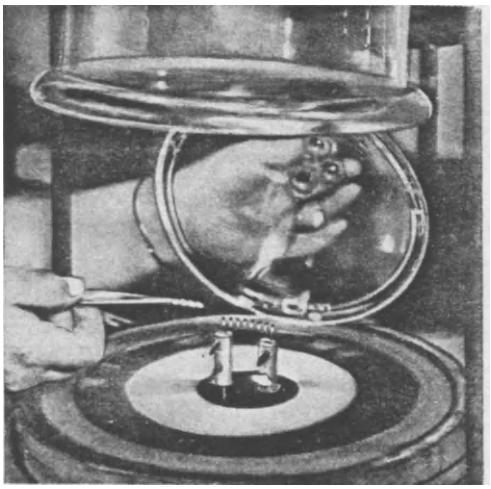


Fig. B 10-216 Aluminizing large reflectors for projection lamps of the type shown in Fig. B 10-161A; loading the W coil with folded Al foil, placing reflector over the source, sealing down the bell-jar (above) (courtesy of GEC) (ROSE)

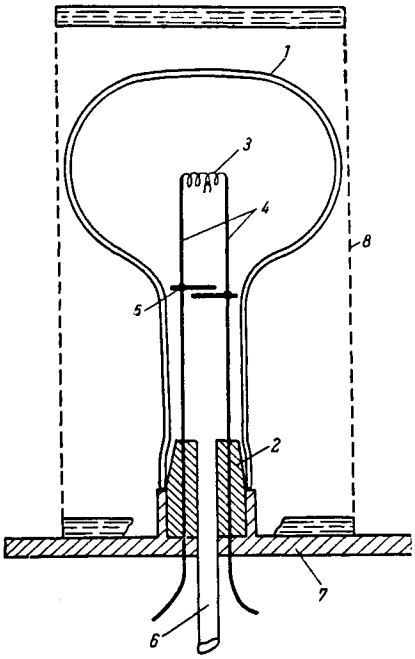


Fig. B 10-217 Device for aluminizing the inside of an envelope with narrow neck

1 envelope; *2* neoprene rubber bung; *3* source (W coil with Al rider); *4* coil supports and current leads; *5* baffle to prevent metalization of the lamp neck; *6* pumping line; *7* baseplate; *8* implosion guard made of transparent thermoplastic material

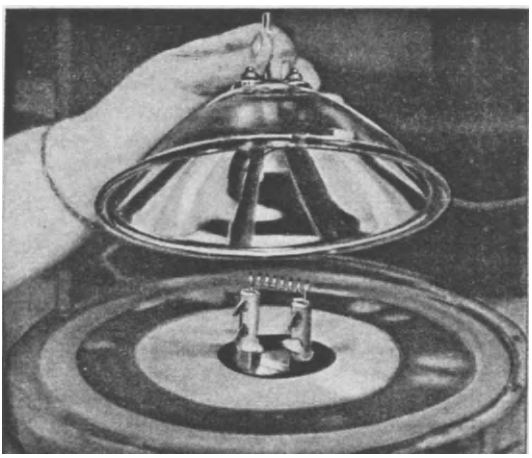


Fig. B 10-218 Removal of aluminized reflector (see Fig. B 10-216) from the evaporation equipment (courtesy of GEC) (ROSE)

work, made by this method; this type is offered commercially for many purposes today.

The low B.P. of Al makes it specially suited to evaporation. An 0.2 μ layer of evaporated Al has a resistivity of $20 \times 10^{-6}\,\Omega$-cm ($= 0.2\,\Omega$ mm^2/m), while the bulk metal has a value of $2.8 \times 10^{-6}\,\Omega$-cm ($= 0.028\,\Omega$ mm^2/m).

Of the chief areas of application the following should be mentioned: lamps with internal reflectors (projection lamps, auto headlights, signal lamps, low-voltage lights for industrial purposes, floodlights, spotlights, railroad headlights, IR lamps, advertisement, sign lamps); optical, especially astronomical, mirrors; coatings for fluorescent screens, 0.05–0.1 μ of Al (see 15.5.V). [10.4]

Because of the technical importance today of internal mirror coatings on glass envelopes (high-reflectance layers of Al), Table T 10–29 gives a complete manufacturing schedule based on the experience of the SYLVANIA ELECTRIC PRODUCTS CO.

Au: as a cathode layer on the glass wall of GEIGER counters for alpha-, beta-, and soft X-rays with energies less than 1 MeV. This increases the cathode electron yield. Similarly, deposition of Pt (see below) by heating a gold-plated or gold-wire-wrapped W wire inserted concentrically in the counter tube. Internal gold coating of IR lamp envelopes (used for cooking); see, e.g., Fig. B 11-23.

Be: primarily for electrostatically screened X-ray windows in glass tubes and for similar purposes on mica disks for ionization chambers to measure X-ray beam intensity.

Bi: used for evaporating an interlayer of about 0.3 μ on Al plates which are to be Se-coated to make selenium rectifiers. Evaporation temperature *ca.* 570° (further details see 7.11, Vol. 1). Also for cathodes of Geiger counters (see Fig. B 7.8-1).

Cd: evaporated on glass for photocells, see 7.6, Vol. 1.

Cr: layers of Cr on glass exhibit relatively poor reflectance in the visible, but are very good in the IR (63% at 2, and 93% at 10 μ wavelength). Because of the high corrosion-resistance of Cr, such mirrors are durable. Cr adheres specially well to glass or quartz, and is therefore used for an interlayer of about 3×10^{-6} cm (300 Å) on which the metal layer proper is deposited by evaporation and in this way a high degree of adherence can be obtained.

Cu: evaporated Cu films are very suitable as interlayers like those of Cr, since Cu adheres firmly to hot glass due to the solubility of cuprous oxide in glass.

Pt: has been employed for internal coating of HV tubes (cyclotrons, beta-trons) with glass envelopes to provide a transparent layer; Pd layers are used analogously for internal metalizing of ceramic-envelope tubes (HURSH). Pt is deposited in Geiger tubes with very corrosive quenching gases like Cl; it is evaporated on the inside of the counter from a concentric W wire wound with fine Pt wire, and the deposit acts as cathode (see Fig. B 4.1-8).

Rh: since Rh films have great durability and chemical inertness, and thus retain constant reflectance values over long periods of time, they were often used before World War I in spite of the relatively poor reflectance (78% for white light). Their use has been much reduced since the development of very corrosion-resistant Al mirrors with SiO_2 protective layers. A special application is evaporation of Rh sheaths on Mo disks and other metal parts to prevent oxidation of these tube electrodes when the mount is sealed into the glass envelope.

Se: for plate rectifier elements, a 40 μ layer of Se is evaporated on Al plates that have been pre-coated with Bi. Quantity production as per apparatus in Figs. B 10-212B or B 7.11-1. Also for photocells, evaporated on Al disks or aluminized glass plates. Further details in 7.11, Vol. 1.

Si: on glass, used as UV mirrors because of high reflectance below 1800 Å.

Note: Metalization of organic materials has assumed increasing importance in evaporation technique, and a few comments relating to this are now given:

[10.4] *Paper* for capacitors is thoroughly vacuum-dried while being gently heated, and is fed past heated crucibles filled with Ag, in large vacuum tanks (see, e.g., GODLEY); this is to produce a very thin layer of Ag whose atoms act as nuclei for condensation of the Zn or Cd deposit which follows immediately afterwards, also from a heated crucible.

Plastics, especially those in the form of foil containing a plasticizer, can only be vacuum-coated if their VP is low and they do not harden by evaporation of plasticizer. Methacrylate (Lucite, Plexiglass) and polystyrene can be readily metalized with Ag Al, Au and Cu, and many others will take Al at least, if they can be degassed to some extent and are placed at least 30–50 cm from the source while a dynamic vacuum of not less than 10^{-4} Torr is maintained by continuous pumping. See BANKROFT, HEPBURN, for more detail.

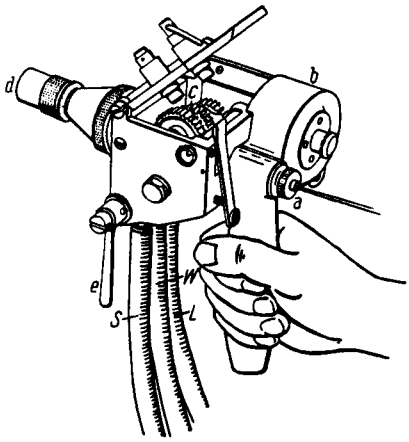
10.4.VI. *Metal Spraying on Glass*

There are two different methods to be distinguished here, differing less in the choice of means than in the end result.

The first method only deals with the provision of an external metalizing which acts as a fairly good conductor and hence as an electrostatic screen for the electrode system of radio and amplifier tubes; there is no chemical bond between the glass and the metal. Adherence is improved by first roughening the glass by grit-blasting (PARKER), or better still, by spraying it with a thin (less than 0.2 mm) layer of Zapon varnish, shellac or adhesive from a spray gun, while the work is rotated continuously at 10–20 cm from the nozzle; the glass should be thoroughly cleaned with alcohol or trichlorethylene beforehand, and all parts not due for spraying should be masked. A good pre-coating solution can be made from 1.2 kg of pot glue dissolved in 5 liters water to which is then added a further 3 liters water at 25°, until a homogeneous paste is obtained; undissolved particles should be removed by filtering through a fine mesh bronze sieve. The solution keeps for 3 months but will not stand freezing.

A special gun is used for spraying metal (Fig. B 10-219) and the material (Al, Sn, Zn, Pb or Cu, usually commercial hard-grade Zn wire 1 mm dia.) is fed through this gun. The metal is melted by an oxyhydrogen flame and is sprayed by compressed air (3 atm gauge) on the work where the individual drops solidify to a conductive coating (see also BALLARD). The glass experiences almost no thermal shock because of the low heat capacity of the drops. On serial production, completed tubes are rotated continuously and fed past the stationary spray gun as in Fig. B 10-220. A Cu wire is first wrapped round the tube just above the base and is sprayed with the glass envelope, thus forming a grounding lead for the metal coating (Fig. B 10-221). The Zn coating on the radio tubes is protected from corrosion by spraying with Al varnish.

In the second process (see, e.g., WOOD), metal coatings designed for soldering are, as it were, chemically combined with a glass substrate by spraying. The glass is well cleaned and is first heated nearly to softening point and then held there while Al is sprayed from a Schoop gun. Apparently, oxide skins which are present on every drop



[10.4]

Fig. B 10-219 Schoop metal-spraying gun for exterior metalizing of vacuum tubes (made by METALLISATOR A.G.)

a wire input; *b* compressed-air turbine for wire feed; *c* drive for wire feed; *d* spray nozzle; *e* control lever for gas and air input; *S*, *W*, *L* oxygen, hydrogen and compressed-air lines

of Al are chemically bonded to the hot glass and this produces so firm a bond between Al and glass that the former can only be removed with difficulty even by filing. On the other hand, the bond has been ascribed to an aluminothermic reaction with glass. In any case, the adherence or bond strength of Al layer to soft glass exceeds 150 kg/cm².

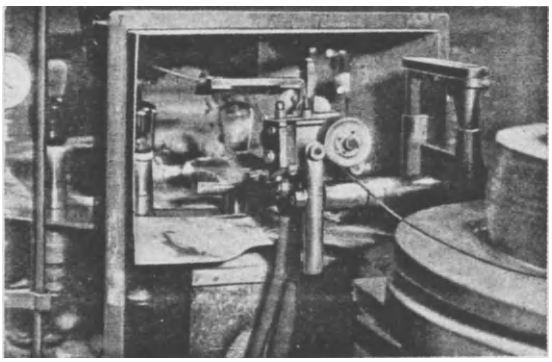


Fig. B 10-220 Automatic metalizing of radio tubes (taken on TELEFUNKEN production line) (cf. also PARKER)

The layers are rough and grainy, and have a much higher electrical resistivity than that of bulk Al. However, neither Zn nor Cu adhere well to glass when applied in this way; alloys of Zn or Si with Al do (PARTRIDGE). When the first layer is applied, which should be about 20 μ thick, care should be taken that no sprayed area of glass cools below 300°. Subsequent thickening can be produced by spraying on the cold surface. If the Al deposits are then sprayed with Cu, which adheres well to Al, the whole deposit can be

soft-soldered to other metal components. Figure B 10-222 shows a Pyrex voltage regulator made by this method; here too, the work was held at 350–400° during Al spraying. Good soldered joints of this type will stand temperatures between —40 and +150°.

[10.4]

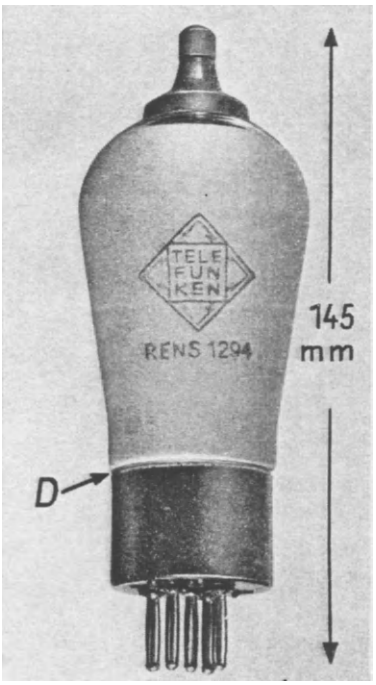


Fig. B 10-221 Radio tube metalized by spray-gun on varnish substrate (RENS 1294, made by TELEFUNKEN)

The spray-coated connecting lead for the electrostatic screening layer can be clearly seen at *D*

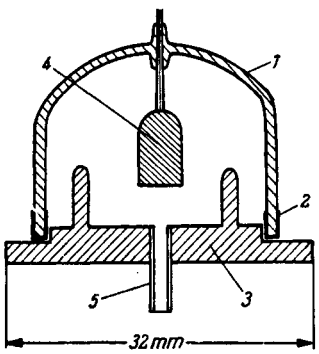


Fig. B 10-222 Hydrogen-filled voltage regulator for 14 kV (cf. SNYDER)

1 hood of Pyrex-type glass; *2* Al and Cu sprayed coating, soldered to Cu baseplate *3*; *4* electrode sealed through *1*; *5* metal pumping line: pure H filling

10.4.VII. *Evaporation of Optical Coatings on Glass in HV*

([2]BLODGETT, H. C. BURGER, DUFOUR, FRY, GREENLAND, [6]HOLLAND, JIOA, ROSS)

These coatings owe their existence to the fact that thin layers of non-metallic and relatively non-absorbing layers on glass give reduced or enhanced reflectance; according to whether the refractive index of the coating is less than or greater than that of the substrate glass. Maxima of either effect occur for coating thicknesses of quarter wavelengths of the incident light, where the average wavelength of non-monochromatic light is taken.

Although this type of coating can be produced purely by wet chemical method (see, e.g., FRY, NICOLL, [4]WEYL), HV evaporation methods have played an increasing part since the end of World War II.

The technique and equipment is little different from those described in 10.4.V. Naturally, the only evaporants involved are those which have, besides the appropriate refractive index mentioned above, the following properties: mechanical strength, insolubility in water, low absorption in the visible, and ease of evaporation without decomposition in HV.

These considerations limit the possible group of materials for antireflexion coatings ($n_{coating}$ less than n_{glass}) primarily to the fluorides, CaF_2 ($n_D = 1.434$), MgF_2 ($n_D = 1.386$) and cryolite Na_3AlF_6 ($n_D = 1.339$); n_D for mirror glass = 1.51, optical SCHOTT glass BK 7, 1.52 approx. For increased reflectance ($n_{coating} > n_{glass}$), the chief material is ZnS ($n_D = 2.3$).

Since the materials named are usually evaporated from the powder, the source holders are generally boats made from strip and directly heated as per Fig. B 10-203, *m*, and [10.4]

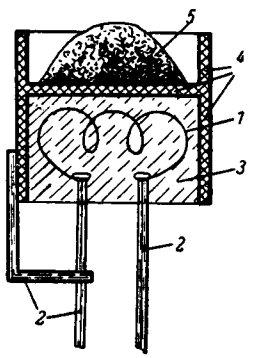


Fig. B 10-222A Evaporation source for powder material designed like a T.H. cup cathode (ALPHEN)

1 W heater coil or Mo heater strip; *2* current leads and support rods of Mo; *3* Al_2O_3 insulation; *4* Mo cylinder bored out above and below; *5* evaporant (powder or chips)

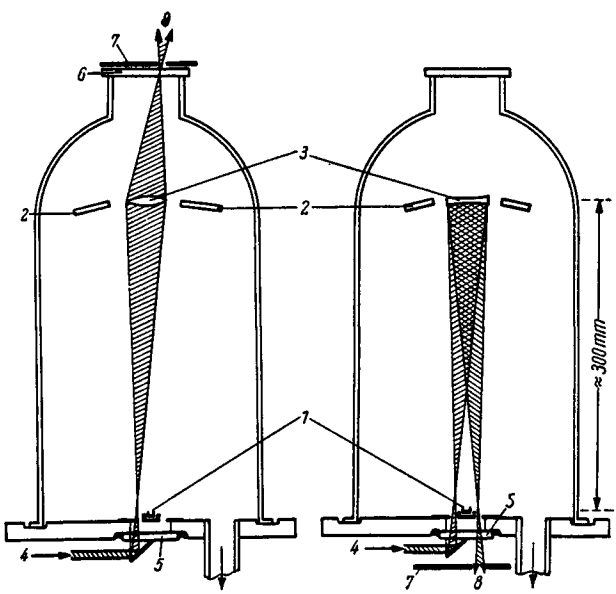
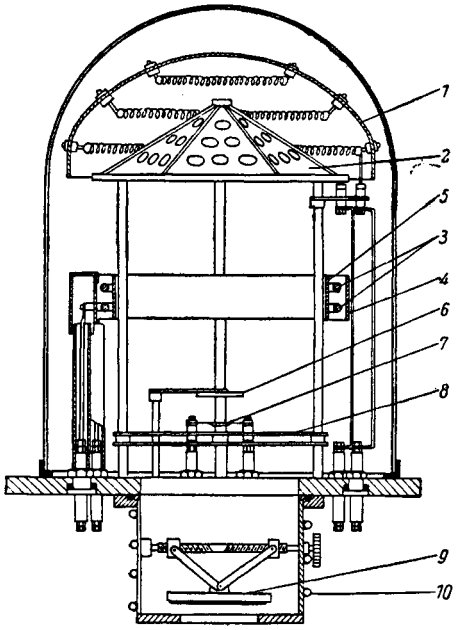


Fig. B 10-223 Arrangement for monitoring evaporated layer thickness during evaporation by measuring transmission or reflexion of a light beam through or by a test-piece (DUFOUR)

Left: transmission measurement, glass lens used as test-piece; *right:* reflexion measurement, using concave mirror as test-piece

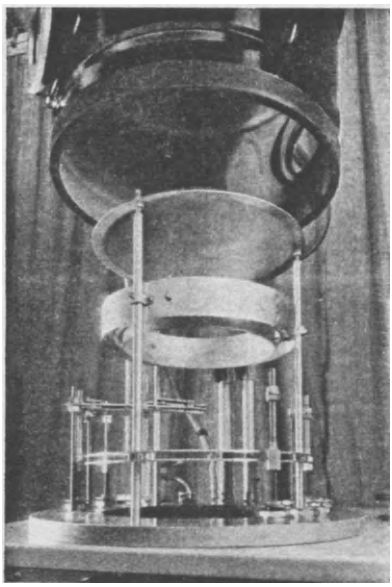
1 point source of evaporant (crucible); *2* glass to be coated is on the surface of an imaginary sphere with source as center; *3* test-piece (glass); *4* monochromatic monitoring light-beam; *5* glass window in baseplate; *6* glass window in dome of bell-jar; *7* diaphragm; *8* exit of beam to photocell

[10.4]



I

II



III

Fig. B 10-223A Apparatus for evaporating anti-reflexion films of MgF_2 on optical lenses ([3, 6]HOLLAND)

I design: *1* radiant heater; *2* lens-holder; *3* two Al ring discharge electrodes; *4* screen to prevent overheating glass wall by ion bombardment from electrodes *3*; *5* screen to prevent evaporation of material on to the discharge electrodes; *6* rotatable baffle to cover source during first degassing; *7* vapor source (heated boat with MgF_2); *8* radiation shield; *9* baffle and HV valve for oil-diffusion pump; *10* water-cooling tube for the pump. II and III photographs of the apparatus with discharge electrodes operating, and opened up (courtesy of EDWARDS HIGH VACUUM LTD., Crawley, Sussex, England)

for fine powder n and o_2; I.H. microfurnaces (Fig. B 10-222A) can also be used. The desired precision in layer thickness can be achieved by the method shown in Fig. B 10-223; a test-body (convergent lens or concave mirror) is exposed to the same vapor stream as the work and reflexion or transmission is measured during evaporation by means of a monochromatic light beam. Many workers have abandoned monitoring on mass-production and fix the thickness by exact weighing of a quantity of evaporant empirically determined as necessary; the whole amount has to be evaporated, of course. The following comments on individual evaporants are of interest:

CaF_2: this material reacts with W and therefore use is often made of heater coils of 0.3 mm W plated with Pt or Rh; a small cylindrical tablet of compacted fluoride *powder* is inserted in the coil. *Crystalline* material tends to spatter when heated *in vacuo* and damages the smooth surface of the coating. [10.4]

MgF_2: when deposited, a 1 or 2 hours baking in air is recommended which should make the film durable. Figure B 10-223A shows an evaporation plant specially made for blooming lenses with MgF_2 and with facilities for radiant heating of the lenses to 250–300° during the process of coating to achieve hard MgF_2 films. This equipment is notable for a particularly effective construction of discharge electrodes (see 10.4.V).

A simple MgF_2 film of thickness $\lambda/4$ reduces reflexion from glass of $n_D = 1.5$ from 4% to 1% (DUFOUR).

Na_3AlF_6: cryolite is the most frequently used fluoride for blooming. According to FRY, one of the better-known processes at LEITZ is as follows: the lenses for coating are thoroughly cleaned in ethanol. Evaporation takes place in a vacuum bell-jar of glass or stainless steel (dia. = 500 mm approx.) at about 10^{-4} Torr, the plant being rather like that in Figs. B 10-208 or B 10-210. The vacuum tank is sealed down with grease-free rubber gasket and pumped out with Hg diffusion pumps without cold-traps. The heaters are two separate series of 8 W boats arranged radially on the baseplate (Fig. B 10-224) and are I.H. by W heater wires in a series circuit. Boats are loaded with precisely weighed amounts (15–20 g/boat) of synthetic cryolite, degassed just below evaporation temperature for 5 minutes before use. The lenses are set in large numbers about 300 mm from the source on a perforated support plate which is magnetically inverted after all evaporant has been used up from the first eight boats. The second series of eight then coat the rear of the lenses. After coating, the lenses are placed in an open air oven and held at about 200°, then one lens from each load is given an abrasion test.

See DUFOUR for a similar procedure using D.H. boats made of 120 μ Mo strip, rotating lens holder, discharge electrode and optical thickness measurement as in Fig. B 10-223.

Recently, blooming of glass with n_D less than 1.57 has been carried out by means of two layers; the first is a sputtered layer of oxide of Ta, Th or Zr, and the second a HV evaporated layer of low refractive index fluoride ([1] HIESINGER).

ZnS: such layers, also vacuum-deposited as a simple quarter-wave coating, raise the reflectance of glass ($n_D = 1.5$) from 4% to 30%, the remainder being transmitted without appreciable absorption. Two ZnS layers on glass, each $\lambda/4$ thick, with MgF_2 interlayer also $\lambda/4$, produce 80% reflectance (DUFOUR). The coatings are, however, relatively soft and have little resistance to mechanical or chemical attack.

CeO_2: this material ($n_D = 2.0$ approx.) has proved effective recently in making highly refractive, hard and inert layers for a double-layer blooming without absorption in the visible.

TiO_2: see [1]HASS for evaporating films of titanium which are then heated for several hours at 400–450° to completely convert them to hard transparent titania films; used for increasing reflectance of quartz-coated Al mirrors. These films have recently been made successfully in a single operation by evaporating TiO in an oxygen atmosphere of $7–10 \times 10^{-5}$ Torr (Swiss Patent 322265). The O_2 is admitted by
[10.4] a needle-valve (cf. Fig. B 20-51) into the evaporation equipment which is continuously evacuated by diffusion pump.

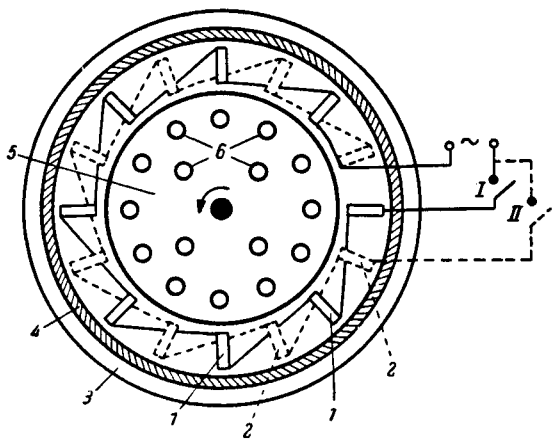


Fig. B 10-224 Plan view of two series of vapor sources for blooming both sides of lenses (FRY)

1 I.H. W boats with heaters in series; *2 idem*, second group; *3* baseplate; *4* rubber gasket; *5* perforated support plate about 30 cm above sources, rotatable and invertable for front and rear coating of lenses *6* (which are fastened to *5*)

10.4.VIII. *Graphite Coating of Glass Surfaces*

(SZYMANOWITZ)

These coatings are used in tube construction mainly for conduction of wall-charges, contacts between glass and deposited metal films, optical blackening to prevent disturbing effects of light reflexion, and to increase thermal radiance of certain glass components. They are often also simply to prevent the tube user from seeing a dirty mount and stained or discolored internal glasswork. It is easy to make them: after the usual glass cleaning (see 10.4.I), a coat of aqueous colloidal graphite is applied by immersion or spraying with a paint spray-gun; "Aquadag", "Hydrokellag" or similar suspensions are used, and their compositions and gas contents can be found in 8.5–4 (Vol. 1). Commercial suspensions should be diluted to a viscosity suited to the method of application with distilled water (about 1 : 1 by weight).

Thin coatings (high-resistance strips for conduction of wall-charges from insulated metal components in amplifier tubes) are discussed in [10]ESPE. They can be made with a fine camel-hair brush. Comb-like graphite electrodes (Fig. B 10-225) can be applied by

template and brush to the inside of a vacuum tube and after heating at 400° in air can be coated with thallium sulfide to make a photo-resistive cell. After evacuation of the tube to protect the top coating from atmospheric corrosion, this gives a very robust construction. The ordinary radio tube envelope (Fig. B 10-226) can be coated by a suitably shaped brush; large TV tubes are coated by a sort of dip process, the "siphon method" sketched in Fig. B 10-227. The graphite suspension is raised to the desired height (close to the picture screen edge of the tube *A*) by means of a supply vessel *F*, adjustable for level, a rubber tube connexion *E* and a rubber stopper *D*. Air in the envelope can escape via an equalization tube *B*. After lowering the level of the graphite [10.4] suspension and removal of the envelope from the apparatus, the graphite coating is next hot-air dried by heating the whole tube for about 2 hours at 450° in an air-oven like that of Fig. B 10-178 (radiation type) to drive off the binder; hot dry air is gently blown in (cf. also Fig. B 15-52A).

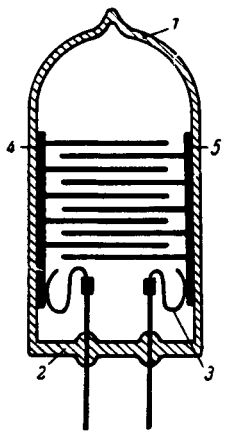


Fig. B 10-225 Comb-shaped graphite electrodes directly applied to inside wall of a tube for thallium sulfide photo-resistive cell (HEWLETT)

1 evacuated tube; *2* foot; *3* contact springs; *4* and *5* graphite electrodes on inner wall, themselves coated with thin, light-sensitive thallium sulfide layer

Figure B 10-228 shows an improved apparatus for coating the inner wall (2) of picture tube cones (1) with graphite fed through a tube (6*a*). The rubber bung (5) carries through its centre two additional concentric tubes (6*b* and 6*c*) through which air which has been dried, heated to about 80° and cleaned by passing through glass filters, enters and leaves during the raising of the suspension level. This avoids condensation of water vapor on the cone wall from the suspension, and hence uneven adherence of the graphite layer, since the suspension would run off any water film without making contact with glass and leave a moist zone uncoated. For the same reason, if the older version (Fig. B 10-227) is used, too rapid a rise of suspension level should be avoided and so should sucking in the suspension by reducing pressure in the envelope (evaporation of water results) instead of forcing it in under pressure by raising the supply vessel (KOHL). Directly after coating, the stopper is left in place and for reliability's sake the flushing-air temperature is increased to 200° and the screen heated externally with a brush flame for about 5 minutes to avoid condensation of water on it. When surface drying of the graphite layer is completed by this process, the envelope is removed from the stopper of the coating unit and the standard heating at 450° is carried out, in order to burn off the organic binder as stated above.

[10.4]

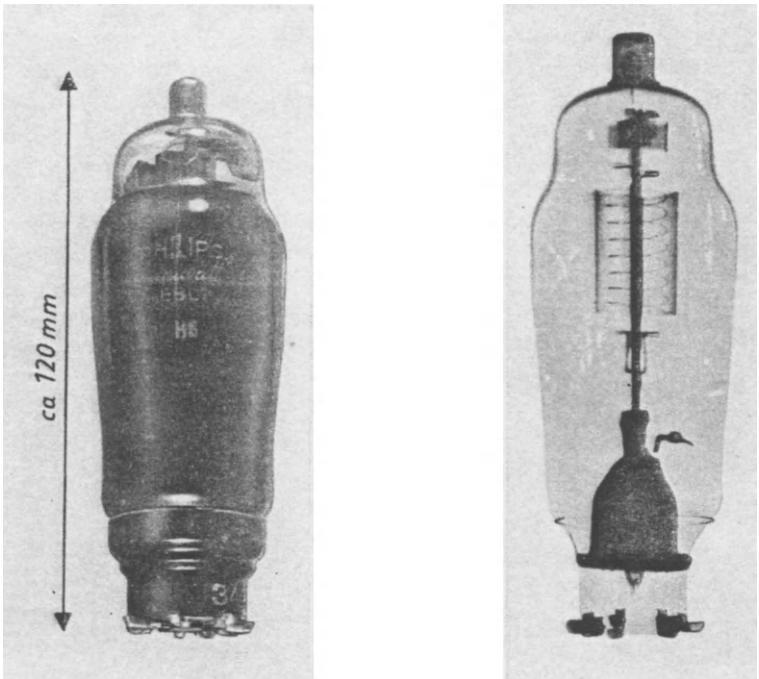


Fig. B 10-226 Radio tubes with internal graphite coating on the glass envelope (PHILIPS tube, type EBL 1); right: X-ray photograph

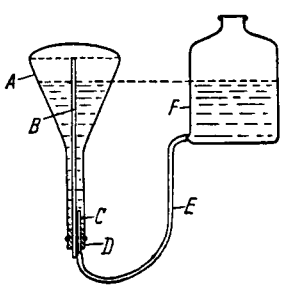


Fig. B 10-227 Application of graphite coatings to TV tubes (ACHESON)

F vessel containing suspension, slowly raised and lowered; *E* rubber tube connexion; *A* TV tube envelope; *B* tube for escape of air displaced; *D* rubber bung with glass tubes *B* and *C*

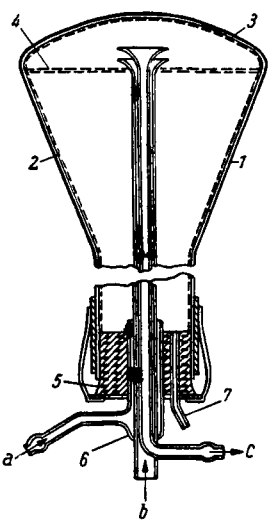


Fig. B 10-228 Improved apparatus for internal coating of TV tubes with a layer of colloidal graphite (KOHL)

1 glass TV tube + cone; *2* graphite layer; *3* picture screen; *4* small gap between screen and graphite layer; *5* rubber bung with holder; *6* arrangement of three concentric glass tubes: *a* for inlet of graphite suspension, *b* for blowing in hot air through a flow splitter, *c* for hot-air outlet; *7* drain tube for residue of suspension

Tube envelopes with defective graphite coatings or that are otherwise unusable can be cleaned off by the method described in 10.4.I, *i*, and then re-used.

Graphite coatings are also applied externally, but must then be protected from mechanical damage by lacquering. An example of this is given in Fig. B 10-229 which shows a blackened vapor cap or dome of a projector lamp, where vaporized W atoms from the filament, carried upwards with the filling gas stream, condense. This is to avoid blackening of the metallic mirror on the inner wall, and of the lamp wall itself. Additionally, the graphite coating prevents unwanted light from the dome. Lacquered outer coatings to prevent "pseudo-high-vacuum" phenomena are applied to the anode arms of Hg-in-glass rectifiers (see Fig. B 10-230). These graphite coatings also have an interesting application in [10.4]

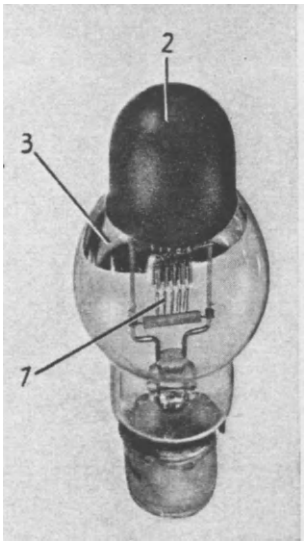


Fig. B 10-229 Projector lamp with blackened cap for condensation of W vapor which convects with the gasfilling (KOTTE) (courtesy of PHILIPS)

1 filament system; *2* condensation cap; *3* inner metallic mirror (cf. also Fig. B 8.5-29, Vol. 1)

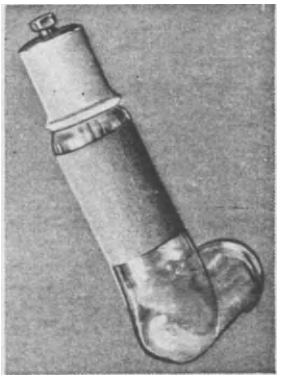


Fig. B 10-230 Lacquered graphite coating on anode arm of Hg-glass rectifier.

the degassing of large-scale glass apparatus, which is hard to heat by any external furnace during evacuation because of size. If glass tubing is coated with graphite, it can easily be heated to 400° with commercial IR lamps and thus degassed quite satisfactorily (STEWART).

Metal coatings can be applied to glass or ceramics to make a vacuum-tight bond and can then be soft-soldered. The method is as follows: it is best to roughen the work surface by grit-blasting with SiC powder, and then brush on a commercial graphite suspension in alcohol to form a thin layer with adequate conductance that is dried firmly on at 200°; Cu is plated on this layer from a sulfate bath (Table T 9.4–4, 8, Vol. 1), where the current density should not exceed 0.03 A/cm² (JAMIESON).

10.4.IX. *Coating Glass with Lacquers, or Varnishes*

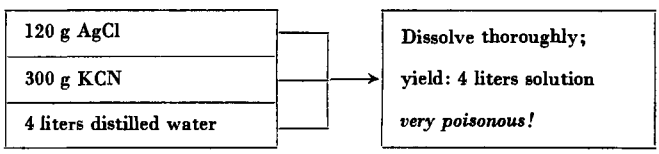
(a) *Conducting varnishes.* These are made by spraying or painting on metal powder in an air-drying varnish. They have the advantage of ease of application but usually have poor electrical conductivity and demand certain precautions to avoid oxide skins on the individual grains and too much varnish carrier, which will produce excessive insulation between conducting particles.

Silvered Cu powder is the most commonc onducting coating since pure Au or Ag powder would be too expensive. The starting material, Cu powder, is generally made by

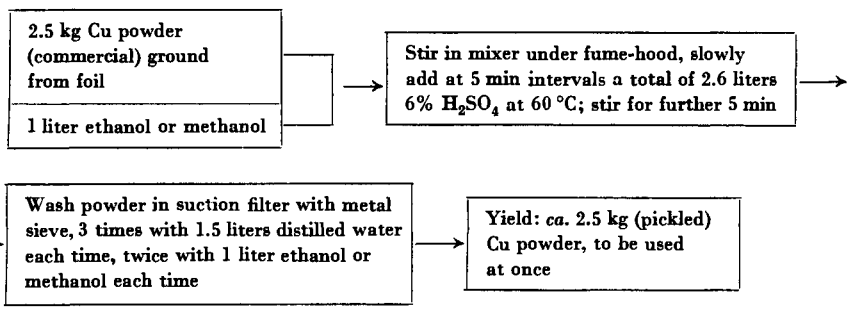
[10.4]

TABLE T 10–30. MANUFACTURE OF SILVER-COATED COPPER POWDER FOR METALIZING GLASS SURFACES

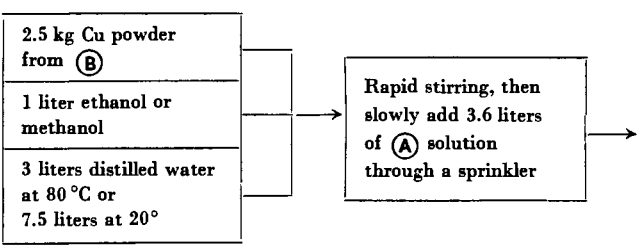
Ⓐ Silvering solution:

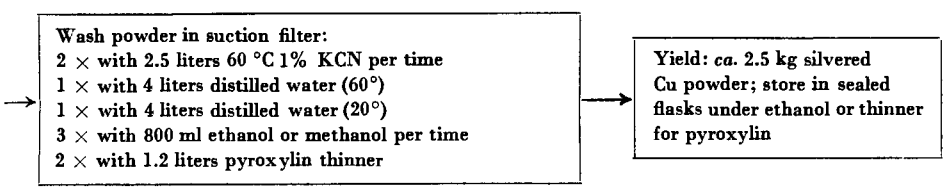


Ⓑ Pickling the powder:


2.5 kg Cu powder (commercial) ground from foil
1 liter ethanol or methanol
Stir in mixer under fume-hood, slowly add at 5 min intervals a total of 2.6 liters 6% H_2SO_4 at 60 °C; stir for further 5 min
Wash powder in suction filter with metal sieve, 3 times with 1.5 liters distilled water each time, twice with 1 liter ethanol or methanol each time
Yield: *ca.* 2.5 kg (pickled) Cu powder, to be used at once

Ⓒ Silvering (immediately after Ⓑ)


2.5 kg Cu powder from Ⓑ
1 liter ethanol or methanol
3 liters distilled water at 80 °C or 7.5 liters at 20°
Rapid stirring, then slowly add 3.6 liters of Ⓐ solution through a sprinkler


Wash powder in suction filter:
2 × with 2.5 liters 60 °C 1% KCN per time
1 × with 4 liters distilled water (60°)
1 × with 4 liters distilled water (20°)
3 × with 800 ml ethanol or methanol per time
2 × with 1.2 liters pyroxylin thinner
Yield: *ca.* 2.5 kg silvered Cu powder; store in sealed flasks under ethanol or thinner for pyroxylin

comminuting thin electrolytic Cu foil and is called "copper bronze" or "flake copper". This is commercially available with particle size about $100 \times 100 \times 3\ \mu^3$. The powder is pickled in H_2SO_4 and then Ag-plated from a silver cyanide solution (Table T 10–30). (Cyanide solutions are extremely poisonous.) Silvered Cu powder must be stored under denatured alcohol or pyroxylin thinner to prevent oxidation. Just before use, the supernatant is decanted and 100 g of the nearly dry powder is well mixed with 80 ml of ordinary colorless pyroxylin (spraying quality) and 20 ml commercial thinner by shaking. The mixture should be employed at once because it will gel in 1–2 days under the influence of the metal powder and become unusable. The given quantities are enough [10.4]

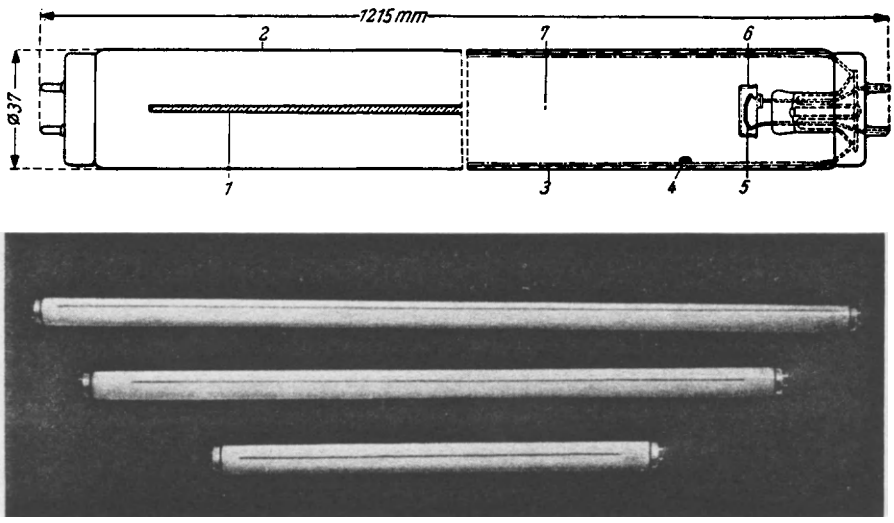


Fig. B 10-231 Low-pressure, mercury-vapor fluorescent tube for mains operation, with paraxial striking coat of conducting lacquer on outer glass wall. The conducting component of the lacquer is silvered Cu powder

Upper figure: design of 40 W lamp (2100 lumens) (from [1]KRATOCHVÍL): *1* striking coat; *2* tube of soda-lime glass; *3* fluorescent coating on inside of tube, totals 4 g, more details see 15.5.X; *4* Hg drop, 50 mg; *5* cathode, a coiled coil of W wire, alkali earth coating deposited by cataphoresis; *6* anode cap, Ni or Ni-plated Fe; *7* Ar filling 3 Torr
Lower figure: manufactured tubes; 20, 25 and 40 W (courtesy of TESLA, Czechoslovakia)

to make the ignition or striking strip for about 250 fluorescent lamps; these strips (Fig. B 10-231) are applied to the outside of the glass tube without special current leads with the aid of a roller stamping device (Fig. B 10-232). This takes place as a rule only after the tube is completed and the fluorescent layer has been fired-on. The coating is air-dried and this can be accelerated by heating to about 140° with a radiant lamp. Adherence to the glass wall and scratch hardness are both excellent. The electrical resistance of such strips is of the order of 1 kΩ.

A whole series of conducting Ag lacquers has recently appeared on the market, designed for a variety of purposes such as metalizing ceramics, mica, glass, plastic, and for coating Al or non-scaling steels. Even without firing-on, they have surface resistances of about 0.02 Ω, and after firing (removal of organic constituents) about 0.01 Ω. For example, Degussa silver glaze (Poliersilber) 242 L is a high-silver liquid preparation

which, after brushing on, gives a very thick Ag coat with one firing; e.g. on glass (fired at *ca.* 540°), hard glass (600–650°) and porcelain (*ca.* 850°). The coat can be brazed with a low-melting silver solder. See DEGUSSA and 10.4.II, for further details on sintered conducting lacquers, or lusters.

See Vol. 1, 3.2, section on applications of W, for making cathodes in glass tubes for Geiger gamma-counters by direct deposition of a W suspension in amyl acetate + collodion by the siphon method (Fig. B 10-227).

(b) *Decorative lacquering.* An example of lacquering for decorative purposes alone is
[10.4] the radio tube metalized with Cu by Schoop gun (10.4.VI); such a tube is given an extra

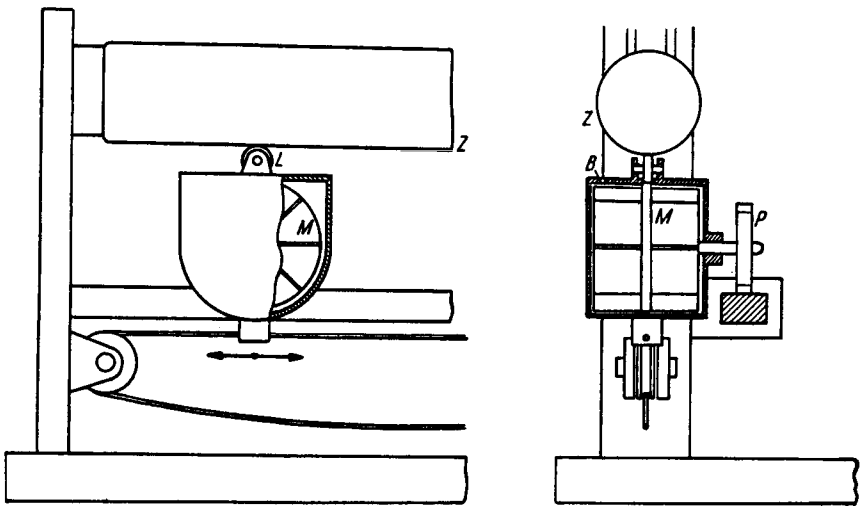


Fig. B 10-232 Roller stamping device for applying the striking coating (see Fig. B 10-231) to discharge lamps working off mains voltage ([2]KRATOCHVÍL)

B container with liquid conducting lacquer; *M* large paddle wheel impeller for conveying lacquer suspension; *P* exterior drive wheel for *M*; *L* small stamping roller, driven by *M* and fed at the rim with lacquer also by *M*; *Z* luminescent tube lamp

spraying with a mixture of so-called "gold bronze" (flake Cu) and nitrocellulose lacquer which produces a golden appearance. This lacquer also should be used immediately after making for the reasons given previously.

For tubes that require a zinc color, the sprayed metal layer is itself sprayed with a lacquer made from 150 g Al powder + 1 liter of diluted colorless varnish + 20 g of titanium white mixed together and ground for 10 hr in a porcelain ball mill.

Opaque decorative coloring on glass tubes is applied usually after the glass has been roughened to improve adherence; commercial nitrocellulose with pigment (often red) is sprayed on. Colored inscriptions or markings can be applied by the well-known transfers (metachromotype) to glass which has been thoroughly cleaned in alcohol. The lettering should be coated with Copal varnish.

(c) Transparent color coatings used to produce selective transmission for certain wavelength ranges: colored, low-power filament lamps, luminous tube lamps, special

dark-room lamps, IR-sensitive photocells (to absorb UV and visible light to reduce fatigue phenomena) are examples. These lamps are first dipped in a solution of *ca.* 150 g gelatine in 1 liter distilled water in which pigment of known absorptivity is mixed, and which contains a few drops of carbolic acid to prevent decay. A coating of cellulose lacquer (25 g celluloid, $^1/_2$ liter acetone, 1 liter amyl acetate) is then applied to protect against mechanical damage.

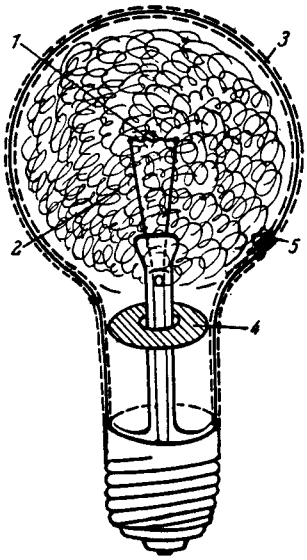


Fig. B 10-233 Photoflash bulb, envelope lacquered inside and out, made by PHILIPS (RIECK)

1 hot filament with explosive paste, when ignited throws off incandescent particles; *2* wire wool, made of 30 μ AlMg wire, 5–7% Mg; *3* glass bulb filled with O_2 to a little below atmospheric, and internally lacquered to extinguish sprayed hot particles, thus avoiding cracking of the bulb. Externally lacquered to retain any fragments if bulb cracks; *4* Al screen; *5* dab of a cobalt salt which is blue if the filling is pure O_2, but goes pink if bulb leaks air + water vapor

[10.4]

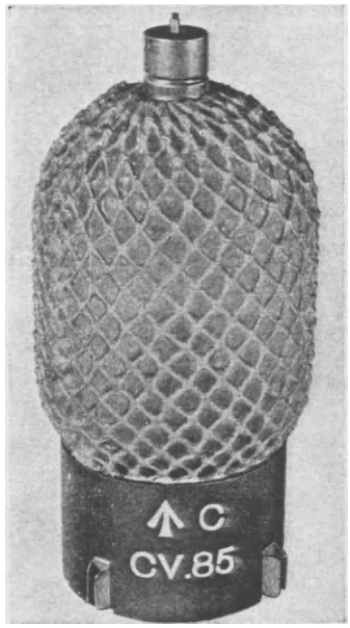


Fig. B 10-234 Shatter-proofing for a pulsed radar transmitter tube with pressure filling (5–7 atm inert gas), consisting of a water-glass coating and wool-yarn mesh cover

(d) *Shatter-proofing.* Both inside and outside of lamps of the type in Fig. B 10-233 are lacquer-coated: these lamps have an O_2 filling and a ball of AlMg wire to produce explosive combustion for high-intensity light emission. The inner wall coat is for extinguishing sprayed hot particles which might crack the envelope. The outer is there to retain, in the event of cracking of the envelope in use, the fragments of glass so that they do not fly off in the form of dangerous splinters.

A still more efficient shatter-proofing is that used during World War II for radar pulsed transmitter tubes filled with 5–7 atm of inert gas; it consists (Fig. B 10-234) of a water-glass coating over which is stretched a close mesh of wool yarn or nylon thread, itself coated with a second layer of water-glass and thus cemented to the substrate.

10.4.X. *Production of Conducting Layers on Glass by Reduction*

([1]BLODGETT, [2]BRITISH THOMSON-HOUSTON, GREEN, [4]WEYL)

If high-lead-oxide glasses with other oxide constituents (such as those of Bi or Sb) are exposed to heat-treatment in H_2, under certain conditions there is superficial reduction of oxide, forming a conducting film. Extensive investigations have been carried out, especially on glasses with high PbO content like those used for X-ray shields and in particular on glass of composition 31% SiO_2, 61% PbO, 8% BaO, similar to "PP" glass in Table T 10–11. The electrical conductivity of reduction layers increases with PbO; oxides of Bi or Sb have an enchancing effect and those of alkalis, B or Al have the reverse effect. [10.4]

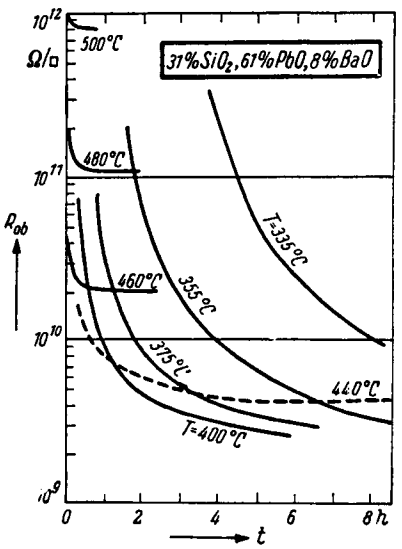


Fig. B 10-234A Fall in surface resistivity R_{ob} (measured at 25°) of a lead glass (61% PbO) with time of heating t in pure H_2; the other parameter is temperature of heating process T ([1]BLODGETT)

The details are as follows: the glass is first dipped in a 35° solution of 1 part concentrated HCl in 100 parts H_2O for 3 minutes, and thus freed of surface PbO which is leached out. Then it is rinsed in distilled water. The surface layer is now pure SiO_2 (10^{-5} cm thick), and this is hardened in an oven at 100–200° for 10 minutes; the higher the temperature the greater the hardness but also the more the SiO_2 film shrinks. After hardening, acid leaching is no longer possible. This treatment not only removes surface impurities and ensures even and reproducible reduction afterwards, but the SiO_2 film, which is easily penetrated by hot H_2 but not by water vapor, acts as a protection both mechanically and chemically for the underlying reduction layer. This film also prevents evaporation of reduced Pb. After this process the glass is heated for several hours at 400° in a pure H_2 atmosphere and acquires a surface resistance of $2–3 \times 10^9 \Omega$ per square (see Fig. B 10-234A).

(*Translator's note*: for the unit "ohms per square", widely used in thin-film work, see this volume, 10.2.XII.)

Still lower values of about 10^3 MΩ or less can be achieved by heating for 16 hours at 350° and then slow (2°/min) heating to 520°. Resistance is measured by two knife electrodes on opposite sides of a square of any desired size (see above). Simply rapid heating to 520° in H_2 (also held for prolonged period) will produce intense blackening by reduction of PbO but will not increase conductance (cf. Fig. B 10-234A). The conducting layer has a thickness of 50–100 Å (5×10^{-7} to 10^{-6} cm) and a specific resistance of 1 kΩ-cm or more. The temperature coefficient is negative ($R_{100}/R_{25} = 60\%$).

High voltage devices of hard glass or ceramic may need a certain degree of surface conductance to provide leakage for electrostatic wall-charges; they can be glazed with the type of Pb-glass discussed. The appropriate glass is ball-milled to pass an 80 mesh/in. sieve. 200 g of this material is then suspended in 150 g amyl acetate and the suspension ball-milled for 24 hours. The suspension is poured over the inner walls of the device and dried at 190° in air. The layer thickness is about 8–12 μ and is fused on; with Corning glass 7060 this would be at 630°, about 60° below softening point. A second layer of about 8 μ is applied and sintered at 570° so that it adheres but remains matt. The same process is used to coat ceramic substrates but with the difference that the suspension is made with a mixture of $^1/_2$ alcohol and $^1/_2$ distilled water. After application on glass or ceramic, the coatings are superficially reduced in H_2 as stated, which produces the value of surface conductivity referred to above. Such layers can dissipate about 0.1 W/in^2. [10.4]

See 10.4.XI for use of surface-conducting glass in HV technology (next section).

10.4.XI. *Production of Superficial Conductance Layers in Glass by Semi-conductor Layers*

KOCÍK has recently given a comprehensive survey of manufacturing techniques of these and other layers on glass. The glass surface is heated to 400–500° and exposed to the effects of the vapor of a metallic salt which, after chemical conversion, forms an adherent, thin and transparent conducting layer. $SnCl_4$ has been shown to be specially suitable for this; it melts at —33°, VP *ca.* 20 Torr at 20°, and about 100 Torr at 56°, 500 Torr at 100°, boils at 113°. The chloride is hot-hydrolysed to the oxide when exposed to water vapor:

$$SnCl_4 + 2\,H_2O = SnO_2 + 4\,HCl.$$

In practice, two processes have proved the best:

(a) Evaporation process (GOMER): this method is specially suited to making conducting layers on internal surfaces of glass, quartz, or glazed ceramic hollow-ware. Small crystals of tin chloride ($SnCl_2 \cdot 2\,H_2O$) are used; they melt at 38°, whereas $SnCl_2$ melts at 247° (VP of 10 Torr at 375°, and 100 Torr at 492°). The crystals are placed in a hard-glass vessel and heated by Bunsen flame to evaporation point; vapor is blown by air or oxygen stream through the device, which is heated at the same time by external furnace to 400°.

One can also heat an aqueous solution of $SnCl_4$ in a boiler (Fig. B 10-234B) and the vapor is fed through the heated glass device and finally condensed in a cooler.

(b) Spray process (MCKINNEY MOCHEL, see also FISCHER). Obviously this process is better for accessible surfaces (external coating) and for glass flats that may be fused on later. An aqueous solution of $SnCl_4$ is made, for example, by taking 100 g $SnCl_4 \cdot 5\,H_2O$ + 50 ml distilled water + 10 ml concentrated HCl (possibly + 0.5 g $SbCl_3$), and often

ethanol addition. This is sprayed from an atomizer as a fine cloud for about 10 or 20 sec on the glass or quartz target, held at 500° or more; in the case of flat disks a device like that in Fig. B 10-234c may be used. Up to 1 mole per cent of $SbCl_3$ may be added (as stated) to increase surface conductivity (FISCHER). Areas not for coating can be stopped

[10.4]

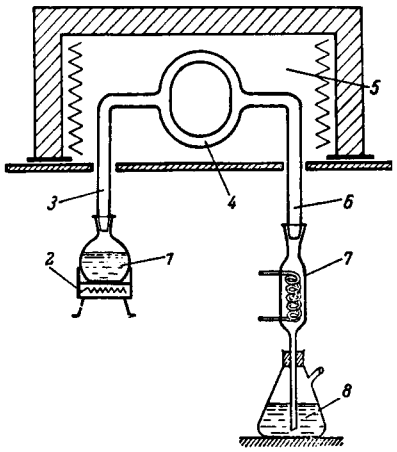


Fig. B 10-234B Set-up for producing superficial conductivity on the internal wall of hollow-ware by forming adherent thin layers of SnO_2

1 Boiler with aqueous solution of $SnCl_4$; *2* hot-plate with sand bath; *3* vapor line; *4* device to be coated (e.g. annular electron gun of cyclotron), heated to 300–500°; *5* external radiation furnace; *6* vapor line; *7* condenser; *8* condensate

off with a layer of colloidal graphite (e.g. Aquadag, see 8.5.IV), which is afterwards removed. To produce homogeneous heating and coating, it is recommended that the work be covered by a hood of sheet material with a window and sliding lid, separated by a few mm from the work. The window is not opened until the glass is up to temper-

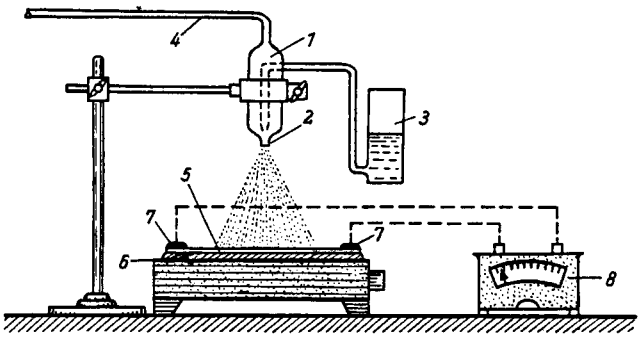


Fig. B 10-234C Apparatus for spraying an aqueous solution of $SnCl_4$ on heated glass to produce a semiconducting layer of SnO_2 (MCKINNEY MOCHEL)

1 atomizer; *2* atomizer nozzle; *3* supply vessel for $SnCl_4$ solution; *4* compressed-air line; *5* work, a glass plate at 30 cm from nozzle; *6* hot-plate; *7* Pt film-strip previously applied by firing for measurement of surface resistance; *8* ohmmeter

ature and the atomizer is working properly, and is closed again after the desired spraying period; the atomizer should not be turned off until this point. The distance of the spraying nozzle from the work should not be too small if the coating is to be even, and should lie between 300 and 500 mm depending on size of target area.

Layers produced by the two methods described consist of Sn silicate with a coating of Sn oxide, or if $SbCl_3$ is added to the spraying solution, of $SnO_2 + Sb_2O_3$. The coatings are very inert chemically, for example to atmospheric moisture, and boiling HNO_3, and withstand heating up to the annealing point of Pyrex (555°) without discoloration or

loss in conductivity; they are also very resistant to abrasion. Thin layers of SnO_2 are practically colorless; as the Sb_2O_3 content rises above 1%, the layer turns increasingly blue. The resistivity of such layers is about $8 \times 10^{-3}\,\Omega$-cm, and can be lowered to a tenth of this by adding 1 mole per cent $SbCl_3$ to the $SnCl_4$. This means that highly transparent layers (0.13–0.4 μ) can be made whose surface ohms per square (see above) will be 600–200.

The thickness of these layers, which show interference colors typical of thin films, can be determined from these colors by observation in white light (FISCHER). Indium electrodes form suitable current-leads to thin semi-conductor films (cf. 7.5), since In wets [10.4] both glass and semi-conductor very well; conducting strips of Pt, applied beforehand to appropriate areas of the glass by firing "platinum bright", are also effective (see 10.4.II). The latter have the advantage that they can be used during coating to monitor the semi-conductor layer resistance continuously (cf. Fig. B 10-234c).

Glass and glazed ceramic hollow-ware internally coated with a conducting surface are used in HV technology for making high-voltage electron tubes (annular electron guns for cyclotrons (Fig. B 12-57)), and for X-ray tubes where the layer will conduct away wall-charges which can become large enough to make a pinhole through the wall and damage the tube; another use of these coatings is conduction of electrostatic charges from the neighborhood of the screen of TV tubes, whose image can otherwise be affected adversely. Conducting translucent glass coatings can also be used for the striking strip on discharge devices (Fig. B 10-231).

A product with the trade name "Electropane" has appeared on the market recently, made by LIBBEY-OWENS-FORD, Toledo, Ohio, USA and by UNION DES VERRERIES MÉCANIQUES BELGES, Charleroi, Belgium. It is a good-quality window-glass generally made by the spraying process with surface conductivity due to a layer of oxide, 0.5 μ thick; it can be used up to 230° (beyond which the resistance rises) both for heating purposes and for a window heated electrically to prevent frosting. Current is supplied through sintered Ag leads. The maximum temperature is 350° ([7]ANON.) and the peak power dissipation in free air is about 1.6 W/cm² of heating surface. The conducting layer on this glass is weather-proof and abrasion-resistant and is almost as chemically inert as the glass. Hollow-ware called "E.C. glass" (electro-conducting) has recently been marketed by CORNING Glass Works, with a conducting layer on the inner surface. CORNING also make conducting glass hollow-ware of the Pyrex type.

10.4.XII. *Insulating Oxide Layers on Glass*

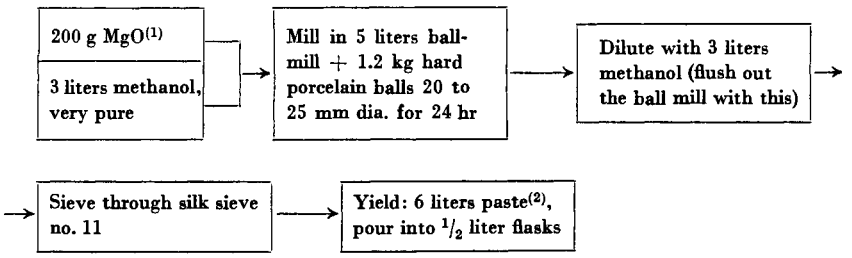
There are cases where evaporation of metal cannot be avoided and it is not possible to baffle it by constructional devices; this may lead to formation of thin conducting layers on glass surfaces.

This arises particularly in the use of glass getters (Chapter 27) in small tubes and frequently also after a period of operation of hot electrodes. It can be very harmful mainly because shunt paths for the grid circuit form across small pinches. The same applies to mica support disks for closely separated voltage leads. The effect can be avoided or at least very much reduced if the surface of the tube-foot is coated with a suspension of MgO between the seal wires or other supports for voltage-carrying electrodes. This coating acts in part purely physically because of its roughness, and

partly chemically by forming insulating compounds, which prevent or hinder formation of a continuous conducting metal film. Table T 10–31 gives a simple recipe for making a MgO insulating paste for *glass* surfaces, generally applied by spraying but also by painting. See Chapter 13 (especially Table T 13–5) for similar suspensions for coating mica,

TABLE T 10–31. INSULATING PASTE FOR SURFACE COATING OF GLASS TUBE-FOOT

[10.4]


200 g MgO(1)
3 liters methanol, very pure
Mill in 5 liters ball-mill + 1.2 kg hard porcelain balls 20 to 25 mm dia. for 24 hr
Dilute with 3 liters methanol (flush out the ball mill with this)
Sieve through silk sieve no. 11
Yield: 6 liters paste(2), pour into 1/2 liter flasks

(1) Made from magnesium carbonate by SCHERING, for example (cf. also Table T 13–5).
(2) Fire hazard. Spray under an extraction hood.

where the carrier must be water, not methanol. Figure B 10-234D shows as an example a small transmitter pentode of very recent type made of hard glass and coated with a layer of MgO on the inside surface of the press between Mo lead-throughs; the two mica support disks for the mount are also coated by the same material.

Fig. B 10-234D Ba-gettered transmitting pentode, hard-glass envelope, with press-foot coated internally between pins with an insulating MgO layer (courtesy of SIEMENS UND HALSKE, type RS 1003)

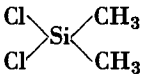
Electrodes supported by MgO-sprayed mica disks. Anode Ni-plated sheet Fe blackened by a preparation of carbon black

10.4.XIII. *Dry Film (Water-repellent Film) Coating on Glass; So-called "Hydrophobic" Coatings*

([1]NORTON, PATNODE, JOHANNSON, HUNTER, SODER)

In this process well-degreased surfaces of ordinary glass, glazed or unglazed silicate ceramics previously stored in air of 50–90% humidity are exposed to organosilicone

vapors, e.g. dimethyldichlorsilane



Suitable mixtures of halogenated silanes have been marketed recently, e.g. "Aquaphob I" of the VEB Chemiewerk Nünchritz (GDR). The same firm makes a silicone oil emulsion (OE E 6008") which, preferably diluted 1:100 to 1:1000 with water, puts a dry film on carefully cleaned glass by dipping process; the glass objects must however be heated for $^1/_2$ hour at 250–300° to fire the silicone film on. [10.4]

This type of treatment produces a reaction with the OH radicals of the gel which under normal conditions is always present on glass, and releases HCl. In the ideal case the result is a surface structure like that of Fig. B 10-235 which is highly water-repellent because of the absence of OH radicals and their replacement by hydrophobic CH_3 (methyl) groups. Even in conditions of high relative humidity no continuous water skin can form on the glass, and this radically improves surface resistivity.

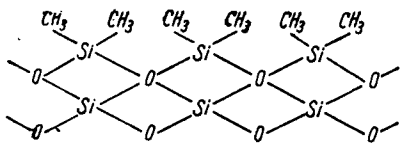


Fig. B 10-235 Surface structure of glass that has acquired a "dry film" from treatment in dimethyl silicone chloride vapor (cf. Fig. B 10-60, curve 6)

The technique of making the films is relatively simple: the glass parts are laid in a container inert to HCl, e.g. glass, which can be sealed and which has an inlet and outlet tube, or in an acid-resistant lacquer-coated wood box with a tightly-sealed lid. Dry air which has bubbled through two or three wash flasks of dimethyldichlorsilane is introduced. Since the VP of this silane is 200 Torr at 20°, the air is adequately charged with its vapor. The reaction with glass proceeds very rapidly and terminates in a few minutes if the vapor can diffuse in every direction. If the reaction volume is large, closed chambers are preferred, made most simply of wood, and the silane is evaporated from drops of an aliquot in a glass dish standing on a hot plate ($\leq 150°$), uniform vapor concentration in the chamber being provided by a closed circulating system. In a space of $1 \times 1 \times 2$ m^3 (2000 liters) the fluid evaporated should not much exceed 50 ml since at higher vapor concentrations methylchlorsilane vapor + air can be exploded by a spark; the danger can be avoided by forcing dry N_2 through the chamber. When the reaction is complete, the chamber before opening is freed of all N_2, silicone vapor and HCl formed by blowing dry air through. The coated parts are allowed to stand in dry air for 24 hours to remove all traces of HCl by evaporation. Health precautions are required because of the HCl vapor, and all open flames or lighted cigarettes should be avoided as always when organic vapors containing Cl are present, since otherwise phosgene ($COCl_2$) is formed (cf. trichlorethylene in 9.4.I, Vol. 1).

In another process, the glass is well cleaned and heated for one hour to 400°. It is cooled below 120° and dipped in a 2% solution of non-volatile dimethylsilicone in tetrachlorethylene of viscosity about 350 centistokes (ŽIŽKA). The glasswork is then removed and the solvent evaporated; the glass is then heated at 180° for about 8 hours to fix the film. (Or one hour at 262°, or 10 minutes at 330°.)

There are also commercial non-hydrolysable preparations containing chlorosilane for coating glass, such as "Dry Film 9987" made by GENERAL ELECTRIC Co. A few drops are applied by a cloth to the clean glass to form an oily coating. All excess is removed by a dry cloth and the surface is polished until dry; the layer thickness is then $2–5 \times 10^{-5}$ cm. Silicone "dry films" are temperature resistant up to 300–400°; they are transparent and do not appreciably absorb light. They can be cleaned with CCl_4 without being attacked and are only destroyed by heating the insulator to 300° for a month or boiling for 1 hour in water. On the other hand, they are at once easily
[10.4] removed by washing in 15% alcoholic solution of KOH. At room temperature an increase in relative humidity from 0 to 100% will reduce the resistivity of a carefully dried but untreated glass surface by 4–5 orders of magnitude (see, e.g., Fig. B 10-60); under the same conditions the surface treated by halogenated silane and then heated will fall by only 2 orders at most. The process is also suitable for improving the surface resistivity of ceramics (see 12.2.XI).

10.4.XIV. *Increasing the Surface Resistance of Glass by Oxidation of Metallic Film Deposits*

When degassing high-voltage tubes with Cu external anodes at high electrode temperatures, it is often impossible to avoid formation of thin evaporated deposits of Cu on the glass wall of the cathode-grid insulation, and this can lead to local softening of the glass in later operation at high frequency. The conductance of these thin films can be nullified by a short break in the pumping process to let in air and "bake" (oxidize) the tube wall to 250° with an external furnace. For more detail see Table T 9.2–8, position 6 and footnote 4. The process is carried out two or three times in very large transmitting tubes.

10.4.XV. *Dealkalizing of Glass Surfaces by SO_2 and Water Vapor to Increase Resistance to Atmospheric Corrosion (Weathering)*

See 10.2.XX, especially Fig. B 10-104.

10.4.XVI. *Internal Coating of Filament Lamp Bulbs with SiO_2 Powder*

(PIPKIN)

Instead of frosting the inside of lamps or "clouding" the glass by adding fluorides (see Table T 10–10B), opal lamps are now made by coating the envelopes with extremely fine SiO_2 powder, a recent process. The grain-size of the SiO_2 particles lies between 4×10^{-7} and 7×10^{-5} cm, averaging between 2 and 4×10^{-5}. In contrast to the two-layer opal glass, these lamps show no loss of strength over clear glass, and have a lower degree of blackening than all other bulbs during their life. They can be run with less N_2 filling (2% instead of 12%) than ordinary lamps, and with a somewhat higher filament temperature without danger of electrical burnout. The SiO_2 deposit is given as 7–13 mg/cm^2. The inner wall of the bulb is etched before application of the coating. No further details of technique are known.

10.4.XVII–XXII. *Chemical Etching of Glass Surfaces*

This process depends primarily on the fact that the silica lattice of glass is dissolved by HF with formation of gas-phase silicon fluoride. According to application, the processes involve HF baths, frosting salts (alkali fluorides) or etching inks.

HF acid is a solution of gaseous HF in water. It should be stored in rubber flasks and handled with great caution, since it, or its vapor, severely attacks the skin and causes suppuration of the mucous membranes. Inhaling vapor should be prevented by masks, or handkerchiefs soaked in soda solution and tied over mouth and nose. The facial skin and hands should be greased, fingernails cut short and gloves or at least fingerstalls should be worn (even when working with very dilute HF). A large vessel of soda solution should always be kept ready near the working space to neutralize the acid. Etching salts are generally less dangerous to handle than HF. The following are details of processes used in practice: [10.4]

10.4.XVII. *Chemical Polishing of Glass*

(HÜBLER)

The most usual baths for this are 1 part by volume water + 1 part by vol. 70% HF; at 60°, 1 minute immersion of Pb-glass or ordinary sheet glass will remove 40–50 mg/cm^2. Addition of H_2SO_4 is recommended to exert a stabilizing effect, although the reaction rate is cut down. Repeated immersion and swilling of the glass helps the polishing process. The amount removed is roughly proportional to time. To compensate for the dilution of HF with prolonged use, the bath temperature can be raised during the immersion process.

10.4.XVIII. *Chemical "Grinding" (Frosting) of Glass Surfaces*

Baths for external frosting of filament lamp bulbs consist of about 7.5 parts by weight of ammonium fluoride and 5 of HF well mixed in a lead-lined wooden bucket, in a warm room. After 12 hours dissolving time, 0.6 parts by weight of soda crystals per part by weight of solution is added. The well-degreased glass bulbs are dipped for 1 min in the clear decanted fluid; bulbs are sometimes previously washed in 30% HF. The etching fluid is then wiped off with a broad brush, and the bulbs are rinsed and wiped dry. Gentle heating of the glass before immersion accelerates the action. In many cases the bulbs are sand-blasted before etching.

A solution for internal frosting of lamp bulbs has the following composition: 42% NH_4HF_2, 7% Dextrin, 20% $BaSO_4$, 3.5% $NaHSO_4$, 27.5% HF. Water should be added till the HF acid content is 18–25%. Parts not due for etching should be stopped off with a thin coat of Picein, wax, or paraffin (wax) which can later be dissolved in turpentine. WOYTACEK gives other recipes for fine and dark frosting.

10.4.XIX. *Chemical Engraving of Glass*

(BIOS, WOYTACEK)

The whole glass surface is first coated with wax, previously dried by heating in molten state at 120° in air or roughing vacuum (oil pump) until completely anhydrous, as shown by no further bubbling. The thickness should be as great as the width of the subsequent engraving line. Wax deposition is carried out by painting or spraying the

hot (120°) wax on the unheated glass. After cooling, the hard wax is scratched with a pointed stylus such as a steel or sewing needle (possibly by machine); for very fine lines of about 3 μ width, a diamond point with a 200 g load is used. This will slightly scratch the glass and the process is therefore really a combination of mechanical and chemical engraving. The chemical part primarily prevents formation of stresses along the engraved line.

For fine diamond engraving, some manufacturers use a mineral pitch lacquer of 200 g pitch, 200 g resin, 200 g ceresin wax and 1200 g turpentine, instead of wax dried at 20° [10.4] for 1–2 hours (BIOS).

After engraving mechanically, HF at 40° is poured over the areas marked from a lead spoon, and washed off after 2 or 3 minutes; or they are painted with a brush of PVC fibers and cold HF three times with 2 minutes intervals. Very fine engraving can be done by spraying a half-and-half mixture of HF acid vapor + air from a lead or Bakelite nozzle; the mixture is obtained by bubbling air at slight positive pressure through 40–60% HF in a closed vessel. The graved parts can also be placed in deaerated containers and exposed to air-free HF vapor over 40–60% HF acid; before etching, the containers are opened and air flushed out by the HF vapor formed, to ensure uniform etching over large areas. One second exposures will produce an etching depth of $\frac{1}{100}$ mm and pro rata (BIOS). After this, the parts should be well washed in running water and then the wax layer removed, partly by careful scraping and partly by washing in benzene; pitch lacquers are dissolved in turpentine and washed away. The engraved zones are matt-white and can be colored with indian ink or pigmented lacquers.

10.4.XX. *Electrolytic Engraving of Glass*

(GUTMAN)

The glass plate is laid in a glass or porcelain trough with a saturated solution of KNO_3, connected to the positive pole of a 110 V D.C. supply (or to one side of 150 V A.C.) (see

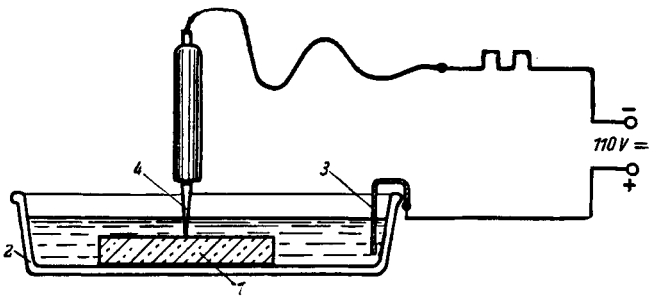


Fig. B 10-236 Electrolytic engraving of glass

1 glass plate to be engraved; *2* glass tank with saturated potassium nitrate solution; *3* Pb strip electrode; *4* Pt stylus

Fig. B 10-236). A graving tool of Pt is connected to the negative side, then placed perpendicularly on the glass flat and slowly moved over the line to be engraved. The current is relatively low, about 1 A, and provided the stylus remains in contact with the glass and is kept in steady motion, a small arc forms at the point of contact due to Na-ion

migration from glass to stylus under the influence of the strong electric field. Where there is no ion flow, as in ion-free glass or pure quartz, the process fails. The arc heat causes two effects: evaporation of electrolyte, which keeps it from direct contact with the stylus, and local heating which produces conchoidal fractures (particles) on a micro-scale at the glass surface, but without detectable stress formation along the graved line. If the stylus is allowed to stop at some point, the arc is rapidly extinguished by ion depletion, and after a prolonged stoppage the glass may break. If the arc is extinguished by lifting the graver, a relatively large electrolytic current begins to flow, 5–10 A at 110 V, and correspondingly large amounts of gas are produced. [10.4]

Lines engraved by this process are very fine and their depth and width can be controlled by suitable choice of conditions. The method has been tested out with equal success on Pyrex, flint, soda-lime-magnesia, and lead glasses.

10.4.XXI. *Inscribing Glass with Inks*

Numbering a mount before sealing into the envelope is most simply done by writing on the pinch with an ordinary stylus and etching ink of the following composition:

Solution I: 36 g sodium fluoride dissolved in 500 ml distilled water, 7 g potassium sulfate added.

Solution II: 500 ml distilled water mixed with 14 g zinc chloride, 65 g concentrated HCl added. Both solutions can be stored in ordinary glass flasks. Before use, equal parts are mixed in a hollowed-out paraffin-wax block and a few drops of indian ink are added. The etching ink dries at room temperature and can be used to make scales on glass.

See WOYTACEK or MÖNCH for other etching inks.

Normal glass inks that adhere without etching the glass can be made by milling for 48 hours a mixture of 34 g purified lamp-black, 250 ml water-glass Na_2SiO_3 (40° Bé) and 185 ml distilled water in a porcelain ball-mill. The product is sieved through a phosphor-bronze sieve (130 mesh/in.), diluted with water-glass to desired viscosity, and is then ready for use.

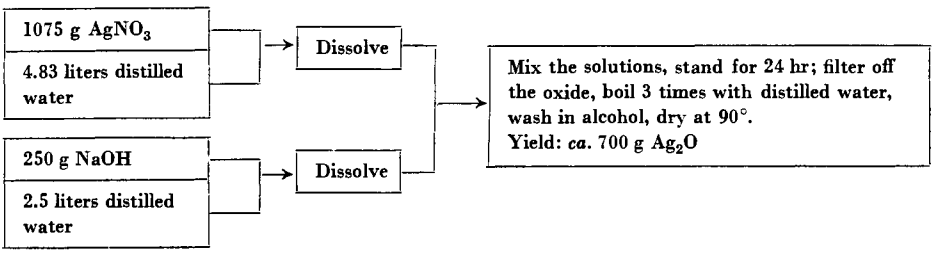
10.4.XXII. *Stamping the Surface of Glass*

Firm's markings or type number can be marked on glass tube envelopes with etching salts; typically such a salt would consist of 10 parts by weight of ammonium fluoride, 2 of sodium chloride, 1 of sodium carbonate, well triturated in a mortar. These salts are available on the market. To moisten the rubber stamp, a glass plate smeared with heavy oil or rubber solution will serve. The stamp is attached to an inflated pad in order to make better contact on a curved surface and after moistening on the glass plate is pressed against the glass surface of the tube, which has been cleaned with cloth soaked in alcohol. Roller stamps are also used. Some etching powder is dusted on the oil stamping with a brush or shaker, and the glass is heated over a small luminous gas-flame. The etching salt is dissolved in the oil and attacks the glass beneath. The etched zone is wiped with a dry linen cloth.

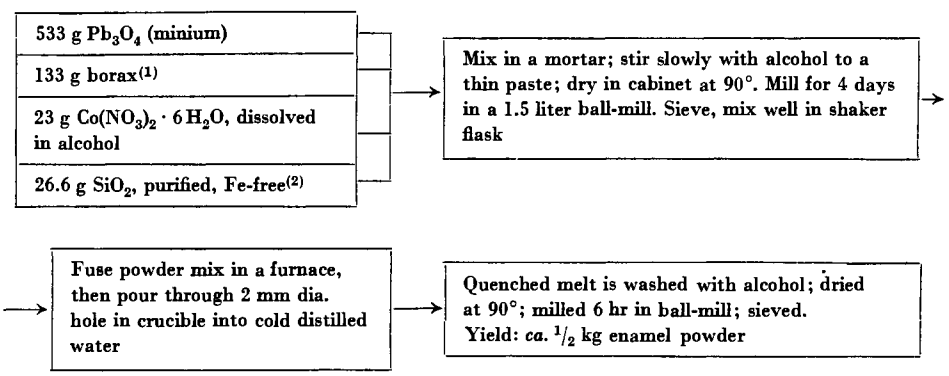
TABLE T 10–32. MANUFACTURE OF SILVER MARKING INK

[10.4]

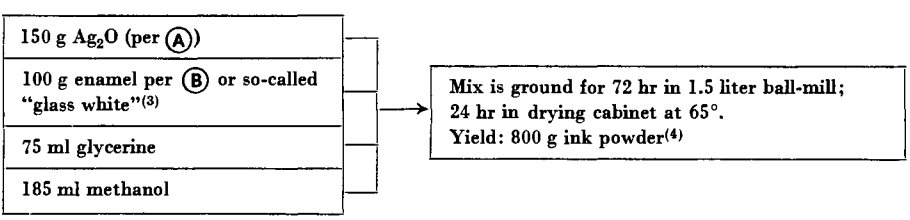
Ⓐ *Making Ag_2O:*


1075 g $AgNO_3$
4.83 liters distilled water
Dissolve
250 g NaOH
2.5 liters distilled water
Dissolve
Mix the solutions, stand for 24 hr; filter off the oxide, boil 3 times with distilled water, wash in alcohol, dry at 90°.
Yield: *ca.* 700 g Ag_2O

Ⓑ *Making enamel powder:*


533 g Pb_3O_4 (minium)
133 g borax(1)
23 g $Co(NO_3)_2 \cdot 6H_2O$, dissolved in alcohol
26.6 g SiO_2, purified, Fe-free(2)
Mix in a mortar; stir slowly with alcohol to a thin paste; dry in cabinet at 90°. Mill for 4 days in a 1.5 liter ball-mill. Sieve, mix well in shaker flask
Fuse powder mix in a furnace, then pour through 2 mm dia. hole in crucible into cold distilled water
Quenched melt is washed with alcohol; dried at 90°; milled 6 hr in ball-mill; sieved.
Yield: *ca.* 1/2 kg enamel powder

Ⓒ *Making the stamping ink:*


150 g Ag_2O (per Ⓐ)
100 g enamel per Ⓑ or so-called "glass white"(3)
75 ml glycerine
185 ml methanol
Mix is ground for 72 hr in 1.5 liter ball-mill; 24 hr in drying cabinet at 65°.
Yield: 800 g ink powder(4)

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(1) Fused, powdered, and ball-milled for 8 days.

(2) Ball-milled for 8 days, sieved, boiled in 10% HCl for several hours and washed 3 times in boiling distilled water till free of Cl ions.

(3) Instead of the "home-made" enamel Ⓑ, one can use the same amount of commercial enamel "Glasweiss" (glass white) made by DEGUSSA, Frankfurt am Main. Analysis shows it to have the following approx. composition: 12% SiO_2, 16% B_2O_3, 58% PbO, 10% SnO_2 (small percentage of this as SnO), 2.2% Al_2O_3, 1.3% CaO, 0.4% alkalis, 0.1% Fe_2O_3. Sintering temp. about 350°.

(4) 300 g ink powder is enough to mark about 100,000 bulbs.

For large-scale industrial purposes, the most common material is "silver marking ink", i.e. fine-ground silicate enamel with high Pb and B content + Ag_2O. Table T 10–32 contains a detailed recipe for making this. The dry powder is stored and every time before use is ground, sieved and mixed with some glycerine in a mortar to form a paste. The marked area of glass must generally be heated with a special gas flame when sealing the envelope on the bulb-sealing machine. Otherwise, the stamped envelopes can be fed through a conveyor furnace before sealing to the electrodes and this also anneals them. The enamel melts on heating and the silver oxide turns to metallic Ag, giving the marking a bright silvery appearance. [10.5]

10.5. Degassing Glass

(BOETTCHER, DAUDT, DUSHMAN, HARRIS, REIMANN, WILLIAMS)

The governing factors in outgassing from glass in vacuum are composition, surface condition, and operating temperature; glass itself has a very low VP, about 10^{-25} to 10^{-15} Torr. Gases are taken up in the body of the glass in a variety of ways during manufacture; as air in preparation of the powder constituents, as decomposition products (mainly H_2O, CO_2) of constituents introduced into the melt not as oxides but as hydrates, hydrated salts, carbonates, nitrates, etc., and finally by absorption into the melt. Even if most of this gas is removed again during the clarification of the melt there still remains a large amount of H_2O, CO_2, and O_2, and smaller amounts of N_2, Ar and some H_2 in the glass after solidification. Besides these gases held in the bulk of the material, the surface has considerable amounts of water-vapor. As explained in 10.2.XX ("Resistance of glass to water"), the glass surface is a silica gel owing to the leaching effects of cleaning water or atmospheric water-vapor picked up in storage. This gel has a low water vapor pressure. If the glass is exposed to hot-water vapor, a definite silica sponge forms with large quantities of mechanically held (occluded) water. The skin which acts as the water source may have a thickness of 50 molecular layers or more (see Table T 10–33). This adsorbed water comes off the tube walls when heated in operation and worsens the vacuum; it must therefore be removed without fail by heating from sealed-off tubes (those not continuously pumped in operation) either before or during the pumping schedule. The heating must proceed at a high enough temperature and for sufficient time at least to ensure that, when the glass wall is raised to the highest tem-

TABLE T 10–33. GAS RELEASED FROM A 200 cm^2 GLASS SURFACE (40 WATT LAMP BULB) ON HEATING IN VACUUM ([2]LANGMUIR)

GAS EVOLVED	AMOUNT OF GAS (mm^3 (NTP))				EQUIVALENT NUMBER OF MOLECULAR LAYERS FOR TOTAL AMOUNT OF GAS
	AFTER 3 HR AT 200 °C	AFTER 1/2 HR AT 200—350 °C	AFTER 1/2 HR AT 350—500 °C	TOTAL	
H_2O	200	100	150	450	55
CO_2	5	15	10	30	4.8
N_2	2	2	1	5	0.9

perature expected in operation, there will be essentially no further water-vapor yield or that if there is any, it is so low that the amount released can be rapidly taken up by

[10.5]

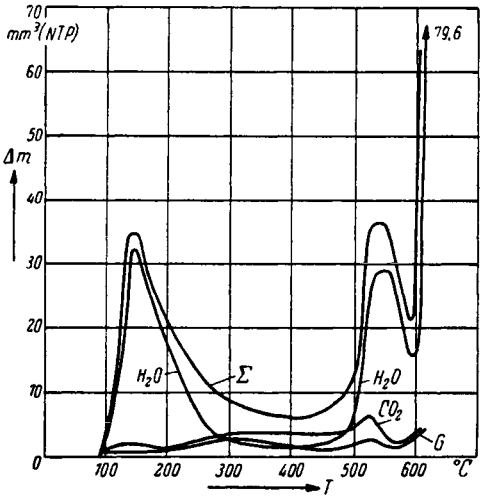


Fig. B 10-237 Gas output Δm from a sodium-silicate glass as a function of degassing temperature T (SHERWOOD)

Note: The abscissa is the temperature at which the 350 cm² glass test-piece was heated *in vacuo*. Each temperature was held for 3 hr and the amount of gas released was determined. CO_2 and H_2O were fractionated by freezing. "G" is the curve for gas not trapped by liquid air (mainly H_2, N_2, O_2, CO). "Σ" represents the total output of gas

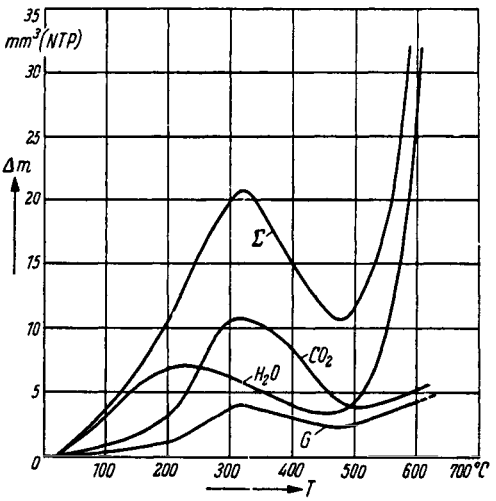


Fig. B 10-238 Gas output Δm of a borosilicate glass (Nonex, Corning No. 7720) as a function of degassing temperature T (SHERWOOD)

See note to Fig. B 10-237.

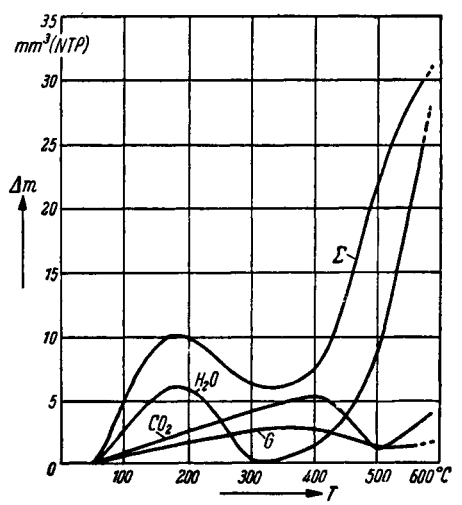


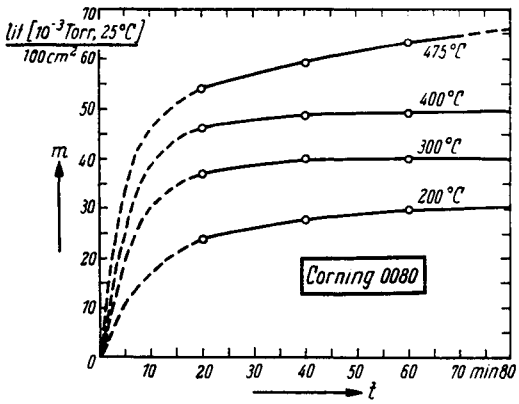
Fig. B 10-239 Gas output Δm of a lead glass as a function of degassing temperature T (SHERWOOD)

See note to Fig. B 10-237.

any getter present. Experimental results correspond by and large with this picture of the situation: if glass is gradually heated in vacuum, at about 150–200°, the majority of the adsorbed gas and the conducting layer of water are removed (Figs. B 10-237 to

B 10-239); above 300° there is a slow dehydration of the underlying source layer and the Si—O bonds reform:

$$\text{Si—OH—OH—Si} = \text{Si—O—Si} \ (+ \text{ water}),$$



[10.5]

Fig. B 10-240 Gas output m of a filament-lamp glass (CORNING 0080, sodium silicate) as a function of time t for which it was heated at temperature T ([3]CARTWRIGHT)

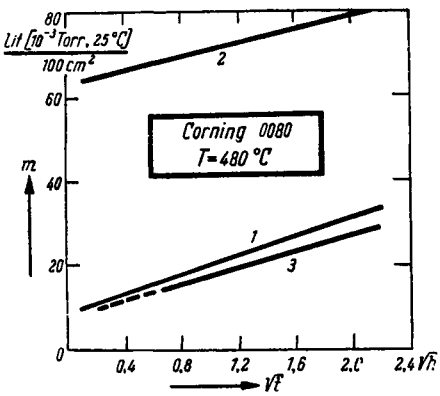


Fig. B 10-240A Water-vapor m released from CORNING glass 0080 at 480° as a function of the square root of the degassing time t (TODD)

1 newly-drawn glass tube; *2* two-year-old glass, washed in water; *3* two-year-old glass washed in 1% HF

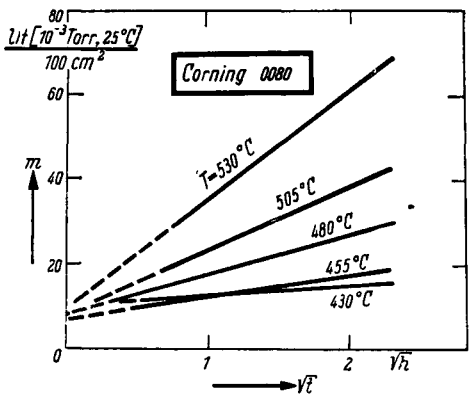


Fig. B 10-240B Water-vapor m released from CORNING glass 0080 washed in 1% HF, at various degassing temperatures T, as a function of the square root of degassing time t (TODD)

so that even after only a few minutes at degassing temperatures between 300° and 400° the subsequent outgassing is very small (Fig. B 10-240). Not until high temperatures have been reached do the gases in the volume of the glass come off, and there is now a continuous outgassing (Fig. B 10-240, upper curve) due to slow outward diffusion of water dissolved in the glass according to the expression

$$m = k_1 \sqrt{t} + k_2,$$

where m is proportional to the square root of time and the ks are constants (Fig. B 10-240A, upper curve). The source of this water vapor is largely the surface layers of glass as shown by comparative measurements on the vapor release from new glass, untreated glass stored for prolonged periods and finally glass that has been stored for a long time and whose surface has been etched with HF acid (Fig. B 10-240A). The water-vapor release is the more rapid the higher the temperature of the glass (Fig. B 10-240B), and the slope of the mass released-time function, or "rate" depends on temperature T

[10.5] $$dm/d\sqrt{t} = C \cdot e^{-A/T}.$$

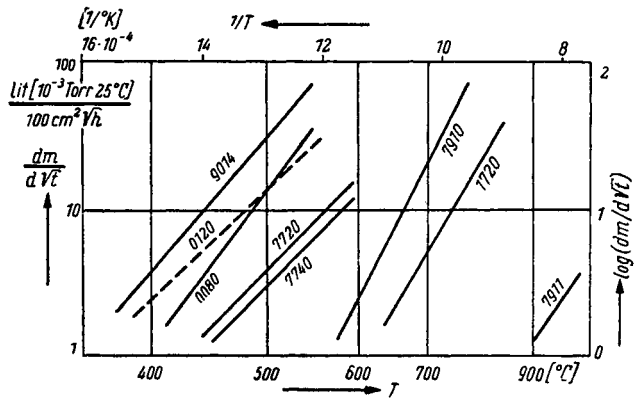


Fig. B 10-240c "Rate" of water vapor release $dm/d(\sqrt{t})$ as a function of temperature T(°C) and of $1/T$(1/°K) for a series of commercial glasses made by CORNING (TODD)

Straight lines will be obtained therefore by plotting log ("rate") against $1/T$

$$\log(dm/d\sqrt{t}) = -A/T + B,$$

where m is the amount of water vapor, t time at temperature T in °K, and A and B constants for the material. As Fig. B 10-240c proves, these functions are straight lines for the individual glasses, and were plotted from measurements on various CORNING technical glasses.

The gas released generally rises with alkali content, and is less the higher the glass was heated during melting in the glassworks (HARRIS). In addition, pre-heating the glass in air reduces outgassing, provided the temperature of heating in vacuum does not appreciably exceed the pre-heat temperature (Fig. B 10-241). This effect holds for several days even if the treated glass is again exposed to the ordinary atmosphere.

The absolute amount of gas given off, as already mentioned, is a strong function of the age of the glass; for example, glasses that have been stored for some years appear to be unsuited for manufacture of photocells with sensitive cathodes (SIMON). The amount of gas is also much dependent on prior cleaning processes, and atmospheric influences under storage. Pb-glasses have less tendency to water absorption (BOETTCHER) than Pb-free glasses, and give off less gas therefore in the range up to 400° (cf. Fig. B 10-239).

Measurements show clearly that temperatures from 100° to 150° are not enough to remove layers of adsorbed gas and above all water films. Therefore in practice one goes for degassing temperatures which are generally 20–60° below the strain point of the glass (cf. Table T 10–5, T_{str} for $\eta = 10^{14.5}$ P, or lower stress-relief temperature). If one excludes gas coming from metal parts of the electrode system and other materials in the tube such as alkali earth carbonates, mica disks, etc., it is generally enough to degas for 20 min in the range 200–475°, since under these conditions glass releases almost all its "free" gas content ([3]CARTWRIGHT). However, in practice (as explained below), large tubes are degassed for much longer, and small tubes which are gettered on the pump later in the schedule are degassed for only a few minutes. It is clear from what has been said, and is a fundamental point in all such glass degassing processes, that too high [10.5]

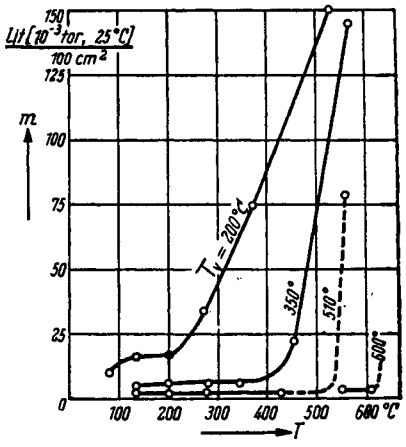


Fig. B 10-241 Gas output[1] m from CORNING glass 7720 (Nonex) as a function of degassing temperature T after 2 hr preheating of the glass in air at various temperatures T_V (SHERWOOD)

[1] Measured as total gas after 1 hr heating at temperature T.

a temperature will under certain conditions do more harm than good (see also REIMANN, [1]LANGMUIR).

As a simple means of monitoring the maximum temperature of the glass wall during pumping, the use of temperature-sensitive dyes and pencils is recommended. They can also be used for determining the peak operating temperature of portions of the glass wall of special concern such as the base section of Hg-filled thyratrons whose operating temperature should not exceed 100°. A. W. FABER (Stein bei Nürnberg) makes the well-known Thermochrome pencil for the range 65–450° in fifteen steps and for 450–670° in three steps. BADISCHE ANILIN- UND SODA-FABRIK, Ludwigshafen am Rhein, make "Thermocolor" dye. For further details see, e.g., GUTHMANN.

An ordinary radio receiver tube gives off in the usual mass-production degassing process, 300–500 mm³ (NTP) of water-vapor, in good agreement with earlier measurements on the gas release from filament-lamp bulbs (Table T 10–33).

Table T 10–33 A contains data on the gas release from various technical glasses during *thorough* degassing of large tubes, individually pumped.

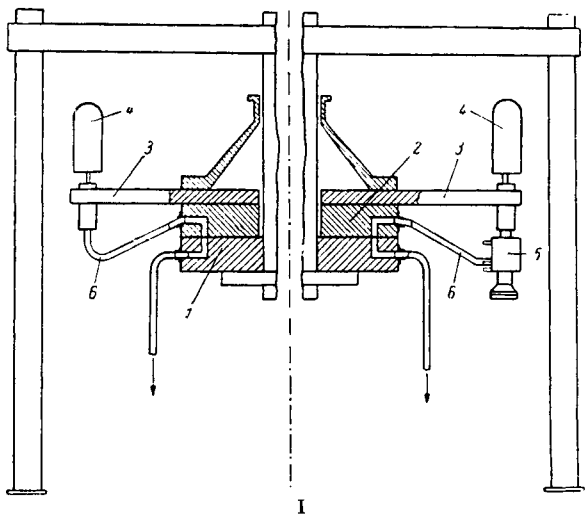
In vacuum technique, degassing of glass, and particularly removal of water vapor from the inside of envelopes, is carried out by heating the assembled tube during the

TABLE T 10-33A. GAS OUTPUT FROM VARIOUS (ELECTRON) TUBES DURING THOROUGH DEGASSING (ARDENNE)

		THÜRINGER GLASSES		LEAD GLASSES	HARD GLASSES
		APPARATUS GLASS	SOFT GLASS		
Transformation temp.	°C	480–580	400–550	410–550	515–750
Most gas released at	°C	320	*ca.* 250	160	350
Condensables	ml/dm²	4.5	19.3		
Non-condensables	ml/dm²	0.48	1.3		
Total	ml/dm²	5.98	20.6		

[10.5]

pumping schedule with external ovens. These ovens may be heated by nichrome or Silit electrical elements (see BENNET for graphical furnace design), or be gas-fired. The



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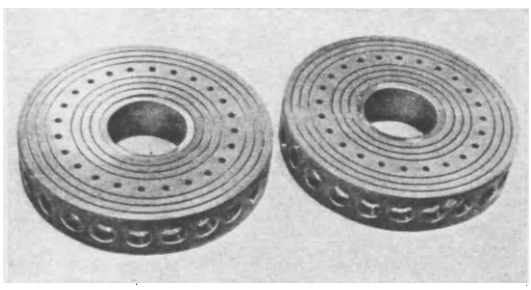


II

Fig. B 10-241 A Vacuum splitter (steel) for pumping table with separate, non-following roughingpump for each station of the table[1]

I principle of construction: right side shown with diffusion pump that rotates with the work; left side shown without diffusion pump, i.e. operates on roughing pump alone; *1* lower fixed-position splitter; *2* upper rotating splitter; *3* carrier arm; *4* tube to be pumped; *5* diffusion pumps; *6* roughing lines.

II photographs of the upper and lower splitters with concentric grooves for castor-oil filling to increase vacuum-tightness of the flat joint surface ([2]KRATOCHVÍL); material: stress-relieved steel with hardened surfaces

[1] By suitable arrangement of holes in the splitters there is a choice of operations besides pumping, such as flushing-gas filling and removal, and final gas-filling (cf. MATHESON)

latter is cheaper and quicker but gives off by-products and consumes oxygen; the working-space air thus deteriorates. Rapidity of temperature rise, peak temperature and holding time are set by the type of glass and the ultimate vacuum required in the tube.

In the case of filament lamps and serial production of small radio tubes, degassing takes place on turntable automatic pumping units (cf. PHILIPS). These have circular manifolds to which tubes are sealed by glass torch or by rubber plugs; for a good seal in the latter case, the hollow plug is filled with compressed air (Fig. B 16-40) or is constructed as per Fig. B 16-41. Generally, the whole manifold rotates with the tubes, all on a sealed metal joint plate (Fig. B 10-241A) connected with the fixed pumping station under the table. The tubes are first roughed out and then pass through a stationary lehr whose entrance and exit are best sealed by an easily removable curtain of asbestos string (see Fig. B 10-242). [10.5]

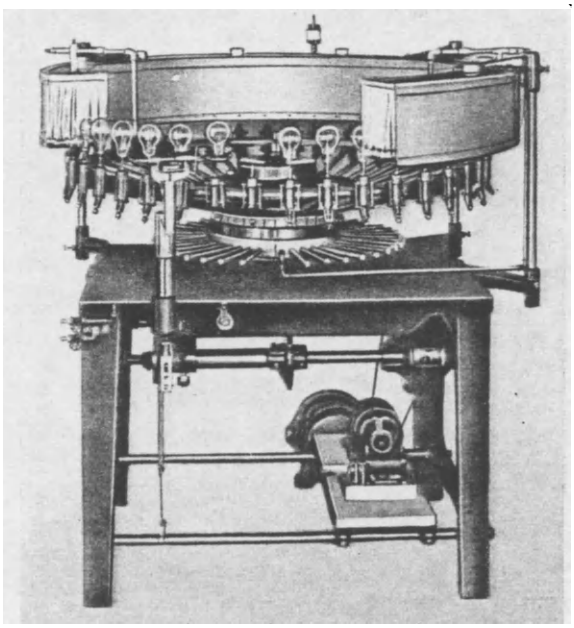


Fig. B 10-242 40-station automatic pumping machine with rotating manifold and large lehr for degassing filament-lamp bulbs (made by GLADITZ GmbH, Schwäbisch-Gmünd)

The glass wall of a tube contains much water, released as vapor during pumping, and this is reduced considerably by an initial air bake (Fig. B 10-241). Therefore, with seal-exhaust (Sealex) machines, the tubes are set up in the machine immediately after sealing in the foot and glass tempering, so that they are *still hot*. In fact, extra burners on the equipment supply additional heat to the glass wall, but not above the point where there would be danger of oxidation of the electrodes or of poisoning the cathode. This removes, in many cases, about half the gas adsorbed and absorbed by the glass walls before the pumping process proper and prevents at least renewed take-up of water vapor from the air which in practice would be unavoidable in cooling and prolonged storage of tubes between bulb-sealing and exhaust. These Sealex machines also save on power and service personnel. Designs are shown in Figs. B 10-145A and B 10-145B.

Where the vacuum requirements are more exacting, only the roughing pump is common to the whole manifold or groups of manifolds, and there is a fine-side pump (and possibly a freezing trap) under each tube, traveling on the manifold with the tube it is pumping. Figure B 10-243 shows the principle of construction of such a turntable machine, and production equipment is shown in Figs. B 10-244 and B 10-244A.

The total heating time in the furnace for filament lamps and small amplifier tubes amounts to about 10–15 minutes with a temperature excursion to 400° for a few minutes. After degassing of glasswork, by external furnace, the metal parts are degassed

[10.5]

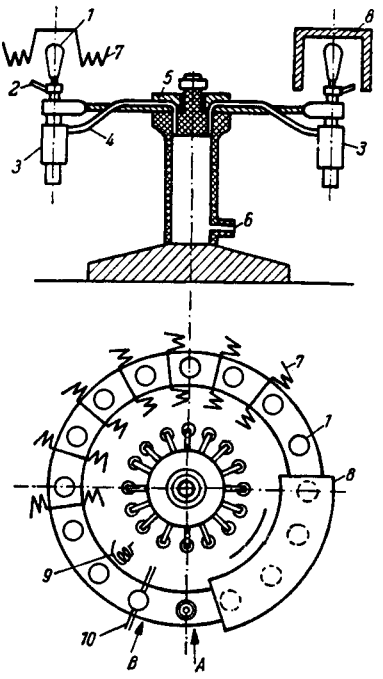


Fig. B 10-243 Design of rotary automatic pumping unit with individual diffusion pumps for each tube, and with common roughing vacuum

A working position for tube to be pumped; *B* removal point of the completed tube. *1* tube; *2* pumping orifice with rubber seal section for the insertion of the exhaust stem of the tube (see also Fig. B 16-41); *3* diffusion pump; *4* roughing line; *5* vacuum splitter like that of Fig. B 10-241A; *6* line to common oil rotary pump; *7* H.F. heater coil as per Figs. B 9.2-28 and B 9.2-29 for degassing electrode parts; *8* electrically or gas-heated lehr for degassing glass envelope; *9* H.F. heater coil as per Fig. B 9.2-30 for flashing getter; *10* gas flames for sealing off exhaust stem

by direct current heating, electron bombardment or H.F. (see 9.2.IV). The hot electrodes radiate heat and therefore the glass is also heated and degassed by this process. Generally, 10^{-2} Torr is taken as good enough vacuum for pumping ordinary filament lamps on a turntable automatic pumping machine, and the ultimate is achieved after seal-off when the lamp is on the forming rack by evaporation of phosphorus (Chapter 27). The procedure for pumping ordinary radio tubes on automatic machines with external oven and H.F. degassing is to exhaust them to about 10^{-3} Torr and getter them by firing Ba by H.F. (Chapter 27) just before seal-off. Sealing off must take place quickly after gettering because the vacuum in the tube may then be better than that in the exhaust line, oil vapor can enter the tube from the pump and may lead to blackening of the oxide cathode surface. With high-power tubes (>50 W) which need laboratory manufacture and with tube constructions that need individual pumping, degassing is carried out on pump-stands with the aid of box or hood furnaces. The tube (or a group of up to 10 or

so small ones on a manifold) is sealed by the exhaust stem to the stand. The degassing ovens are often simply made from asbestos sheet. Better thermal lagging is provided by double-walled asbestos or metal sheet ovens, with the sheets separated by about 5 cm. The insulation is air or Al foil. In this construction care should be taken that the stand-offs between inner and outer walls have as low a thermal conductance as possible (small cross-section, Invar). Such ovens have to be lifted frequently and should be light; the best way is to make frames of angle iron with walls of Al sheet. Al frames should not be used because Al has low hot-strength.

[10.5]

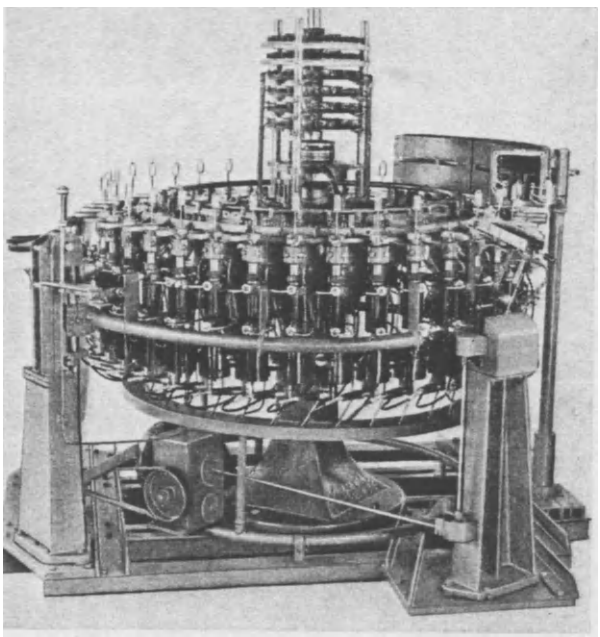


Fig. B 10-244 Automatic pumping unit for miniature radio tubes with 36 water-cooled Hg-diffusion pumps and lehrs (made by SCHMIDT UND KLEINBERG GmbH, Neu-Ulm, type PA 36D)

Pumping table dia. 1.4 m, output 360/hr at 6 min exhaust time per tube

Figure B 10-245A shows typical double pumping-stands with electrical box furnaces that can be hoisted, and with control panels used for degassing and forming of small short wave tubes. Figures B 10-246 to B 10-246B show pumping stands for degassing individual high-power transmitter tubes, HV rectifiers and X-ray tubes, using large electrically heated hood furnaces and a control desk separated from the pump.

All-glass transmitter tubes of medium power-rating with soft-glass envelopes are heated for 1 hr at 400–420°, rising from room to 400° in about 10 min: *X-ray tubes, HV switching tubes or rectifiers* and other large glass-envelope tubes must be brought slowly to peak temperature in 1–2 hours because of the danger of fracture, and must often be held at this temperature for up to 24 hours. The peak temperature for *hard glasses* is 480–500°.

The maximum degassing temperature is basically determined by the danger of collapse under atmospheric pressure, especially with large glass envelopes. The permissible degassing temperature can be substantially raised if the internal volume of the electric degassing furnace is pumped out to a few Torr. Higher vacuum should be avoided so that no short-circuiting gas discharges take place between the turns of the

[10.5]

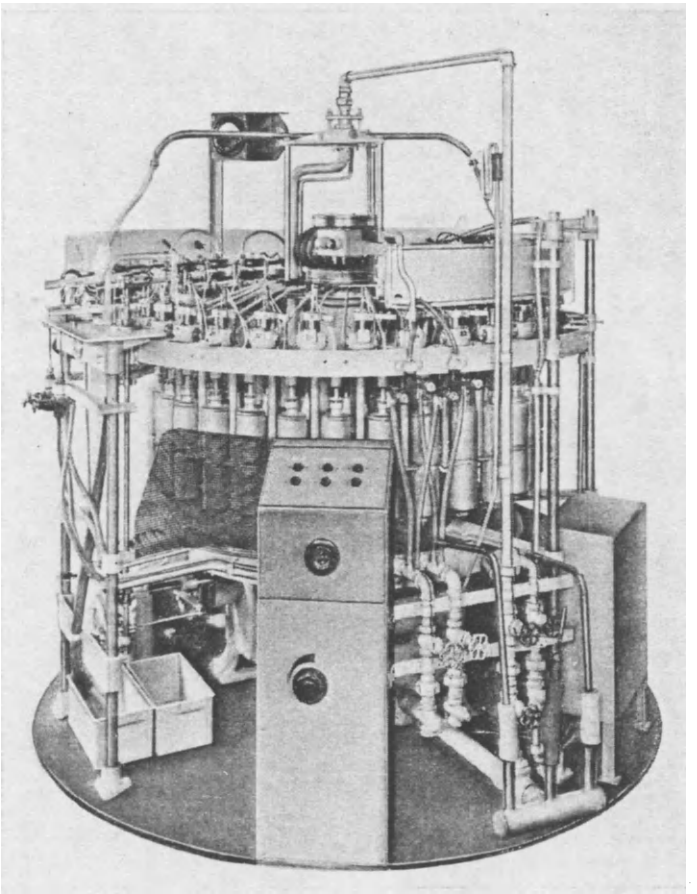
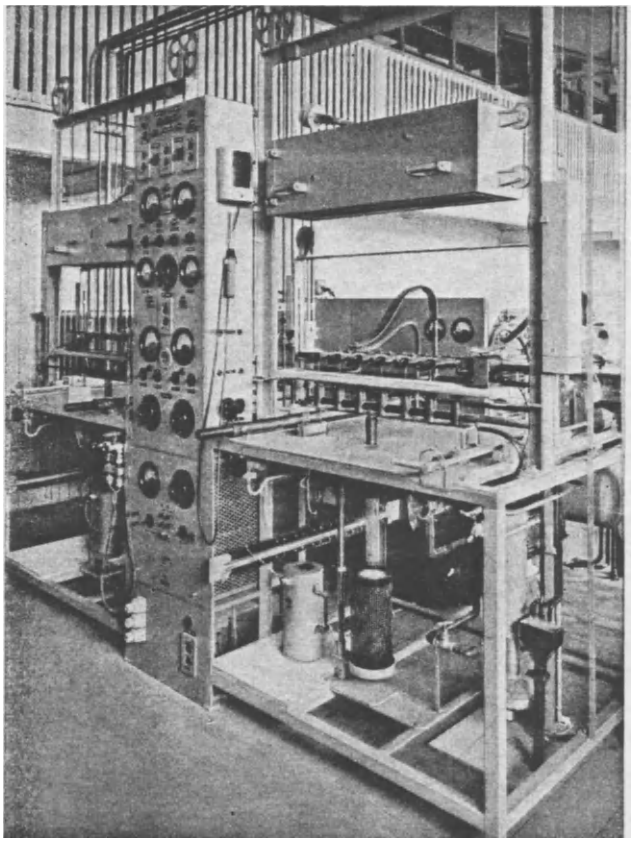


Fig. B 10-244A Automatic pumping unit for radio tubes with 30 Hg-diffusion pumps and gas-heated lehr for 400° (made by ELSTROJ-Prague, type 11 S). Pump table dia. 2 meters, stepping interval 8–16 sec, 225–450/hr

heating elements inside the degassing furnace shell, and for the same reason the heater element voltage should not exceed 70 V r. m. s. Figure B 10-247 shows the design of such a degassing furnace in which it is possible to raise the degassing temperature of large soft-glass tubes (Hg rectifiers) by about 100° and hard-glass tubes by about 80° for the same degassing times. An additional advantage of this for tubes with Cu electrodes (e.g. water-cooled external anodes of high-power transmitter tubes) is that high

degassing temperatures completely reduce Cu surfaces without further treatment (see, e.g., 5.4, Vol. 1, p. 293). This degassing method in evacuated external ovens has proved specially useful for tubes with Housekeeper seals (Chapter 30), since the Cu rings may collapse at degassing temperatures in ordinary unpumped ovens and even when the glass wall is able to withstand these temperatures. The Cu ring periphery forms an annular dent and is so to speak upset, or axially crushed.



[10.5]

Fig. B 10-245 Twin pumping station for 2×6 low-power short-wave tubes with drop-over electric box furnaces for glass degassing, and common central control panel (courtesy of BROWN BOVERI)

Figure B 10-247A shows another design of degassing equipment in which the tube can be degassed under internal and also external vacuum at up to 700°; this has proved specially valuable for hard-glass USW tubes with Mo ring seals.

When degassing large glass envelopes by external furnace, it is recommended that glass freezing traps with liquid air be placed between tube and Hg diffusion pump only after reaching peak furnace temperature, i.e. when most of the water vapor released has been removed, and to work with gas ballast pumps to avoid contamination of the pump oil by water.

While it is desirable to undertake furnace degassing and electron bombardment simultaneously, the danger of glass electrolysis makes this possible only with tubes whose lead-throughs are sealed in far apart from each other, and therefore as a rule not with pinch-tubes. The furnace temperature has to be lowered because of additional radiant heating of the glass from within and gas bursts have to be watched for; they are detectable by a luminous gas discharge.

Another type of system has been developed recently (Figs. B 10-248, B 10-249) for making large TV tubes, for aluminizing of fluorescent lamp screens (see Chapter 15),

[10.5]

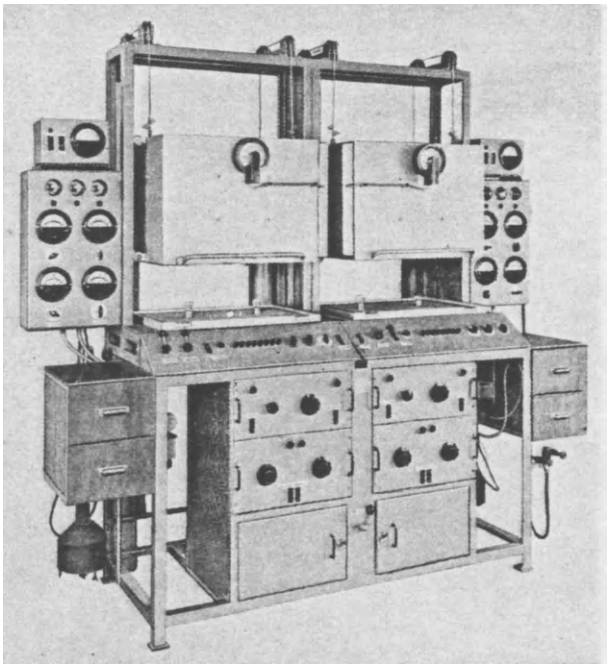
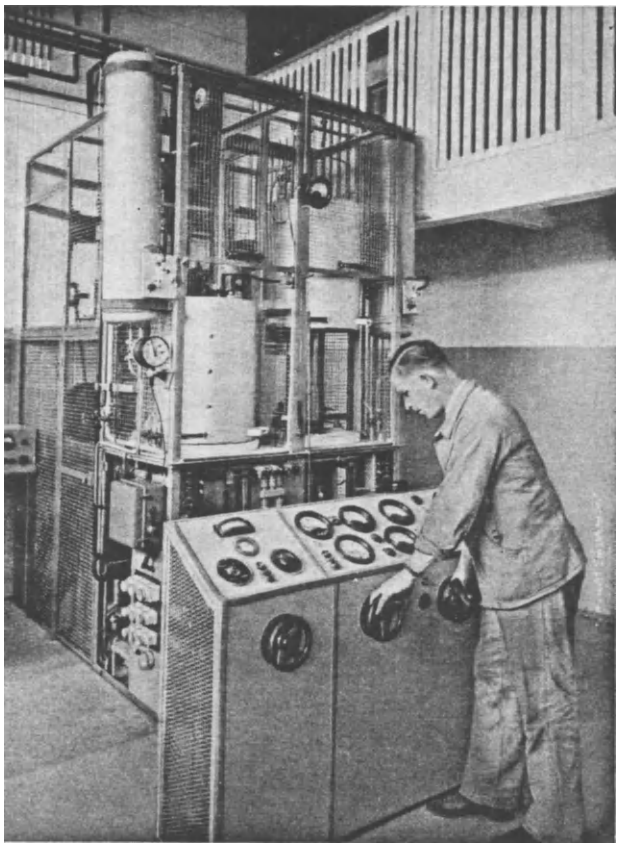


Fig. B 10-245A Twin pumping stand for small tubes, made by TESLA-Elektrosignal-Elstroj, with electrically heated box furnaces (WEINZETTL)

automobile lamp reflectors (Fig. B 10-216) and IR lamp envelopes (Fig. B 10-217), and for pumping medium-power transmitter tubes. The system employs pumping stands running on wheels ("trolleys") on which are mounted not only the tube but also a two-stage rotary oil gas-ballast pump, with a throughput of *ca.* 5 m^3/hr in the case of 17 in. TV tubes (10^{-1} Torr in 4 min); oil diffusion pump (speed 50–100 liters/sec at 10^{-5} Torr); vacuum gauge; valves; water-pump with filter whose input comes from a fresh-water channel running between the rails of the trolley-way and after circulation is returned to a second channel; H.F. degassing work-coil; control and monitoring equipment. These pumping trolleys are formed on rails into two straight, countercurrent in-line systems (WARREN; Figs. B 10-250 to B 10-250B) with turn-round sections, on to which they are driven after pre-evacuation of the tube in the degassing lehr that takes up

almost two-thirds of the whole trolley-way (Fig. B 10-251). Afterwards they travel by stages through the other equipment (voltage supply for cathode forming, H.F. generator final testing unit) in a predetermined program with corresponding switches and contacts. At the end of the return run the exhaust stems are sealed off. This process has



[10.5]

Fig. B 10-246 Individual pumping stand for large transmitter and other high-voltage tubes, with hood oven and separate control panel (courtesy of BROWN BOVERI)

The oven is hoisted after the degassing of the glass wall and, most important, during electrode degassing by electron bombardment

the advantage that if any tube is damaged (implosion, leaks, individual pump failure, etc.) the schedule for the other valuable tubes is in no way affected. The trolley with the damaged tube can simply be switched out (usually automatically) or can be removed to one side during a pause between stages and replaced by blank bridging device. For essential overhauling of pumps and other components, the trolley can be quickly taken out and replaced by a reserve.

How many trolleys are needed for such a system can be seen from the following case taken from practice: exact laboratory investigations show that the overall pumping

time must be at least 90 minutes. The system should produce 1 tube/min. Since tube removal and replacement requires 1 min/tube and cool-down time for the diffusion pump for safe inlet of air is 3 minutes, the number of trolleys is 94. One can, it is true, eliminate the last three cooling positions if the diffusion pumps are closed off by valves and only reconnected by a changeover valve (Fig. B 10-249) after roughing out of the

[10.5]

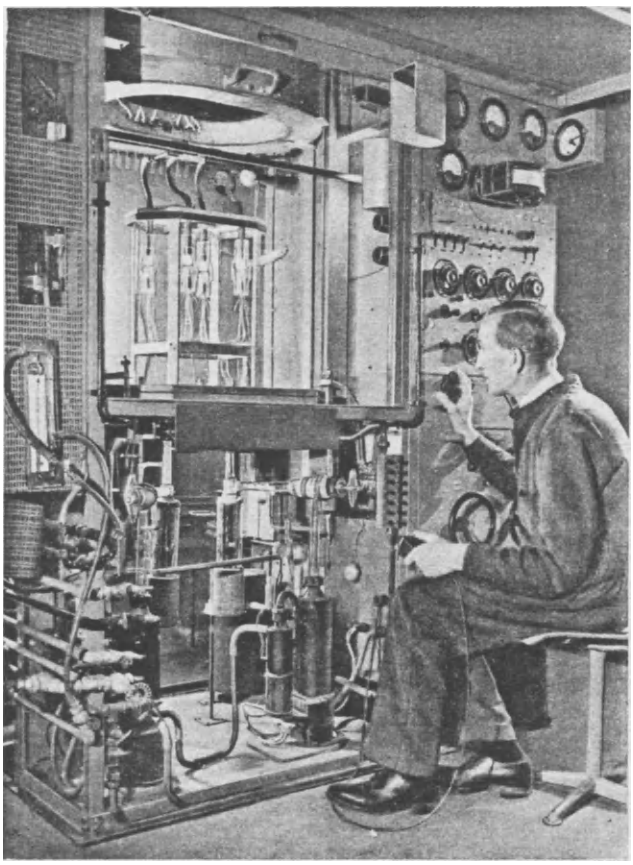


Fig. B 10-246A Pumping stand with hood oven raised during electron bombardment; the oven is used to degas 2×2 X-ray tubes (courtesy of PHILIPS) (see [13]ANON.)

tube by the fore-pump; but this does not appear to be a sound procedure on mass-production with long pumping times (long trolley-ways) because of the susceptibility of the valve to damage (glass splinters) (REICH).

After degassing glass envelopes by external oven, and heating the electrodes, the inner glass surface often exhibits local surface conductance which can reach unacceptable proportions, especially in H.F. transmitter tubes. This conductance can, in later operation, lead to the glass wall becoming heated locally by the H.F. field to the point where "hot spots" form. At these points the wall may collapse under external pressure.

The cause of the phenomenon is condensation of a thin grease layer, evaporated from the heated metal electrodes on the wall, and in spite of all precautions this cannot always be avoided. During the degassing process in the oven, the grease decomposes to conducting carbon. The hot spots produced by this can, however, be removed; when the overall degassing cycle is complete, air is let in and the temperature somewhat increased and held for $^1/_2$ hr. The whole degassing process is then repeated (Table T 9.2–8, No. 6). Cu-anode, hard-glass transmitter tubes can be degassed up to 560° by using an evacuated external furnace (see above); it is sufficient here to let in air to only 4 Torr for a short time during the degassing process, lowering the temperature to 500°, and [10.5] then pumping out, and raising the degassing furnace temperature to the maximum permitted (about 560°). This certainly oxidizes the Cu parts superficially, but after

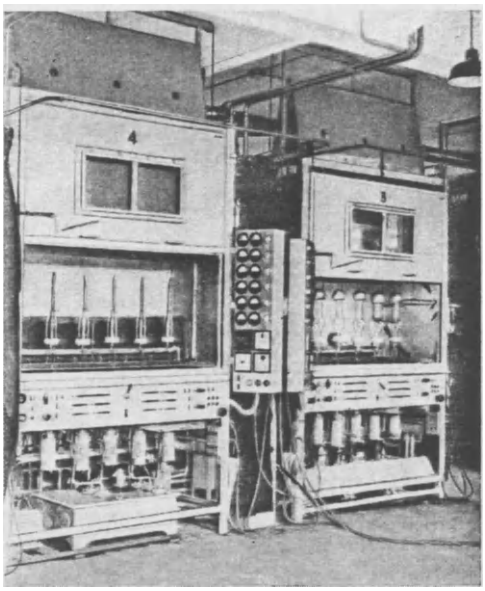


Fig. B 10-246B Twin pumping cabinets for X-ray tubes, with lead shields and each provided with five independent diffusion and rotary oil pumps (courtesy of SIEMENS-REINIGER-WERKE, Erlangen)

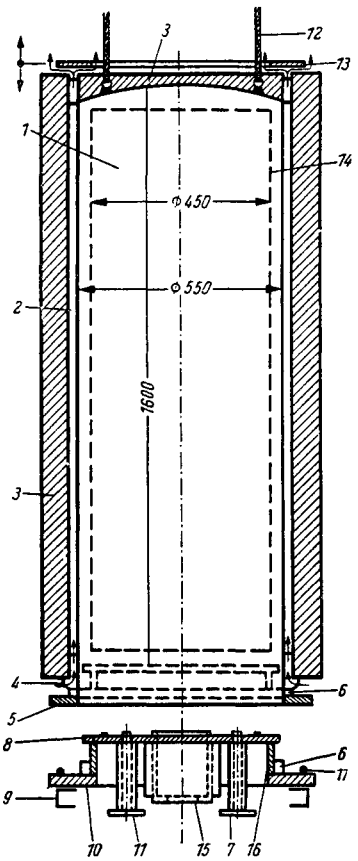
renewed pumping out to HV at 560° they are reduced and very uniformly cleaned. Previous stains on the Cu are removed by this oxidation-reduction process. It is recommended that large tubes be given the air-inlet treatment two or three times.

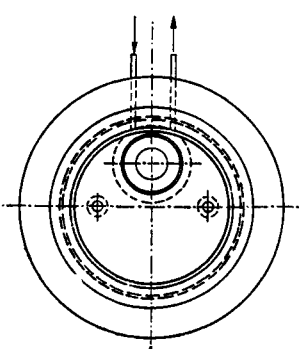
With low-capacity pumps and in laboratory work, care should be taken in the glass degassing process that not only the electron tube but also the pumping line be degassed. The simplest way is to flame the glass line with a "cool" bright luminous gas flame to about 350°, or to paint it with a thermally absorbent graphite layer (10.4.VIII) and heat with IR lamps (STEWART).

Particular attention has to be paid to gas released from glass when sealing off the exhaust stem. This is either done by hand (Fig. B 10-252) or, in the case of small tubes on automatic machines, by cross-fires. Stems of small radio tubes and lamps and with O.D. of 4 mm, 0.8 mm wall, can be automatically sealed off on the machine at the end of the pumping schedule; TV tubes with stem diameters above 6 mm have to be sealed

off by hand. The seal-off temperature is necessarily above 650°, and there is a considerable and unavoidable release of gas due to decomposition of the glass (cf. Figs. B 10-237 to B 10-239). In order to release the least possible amount into the sealed-off tube, the seal-off zone should be specially well degassed beforehand with the torch. The amount

[10.5]





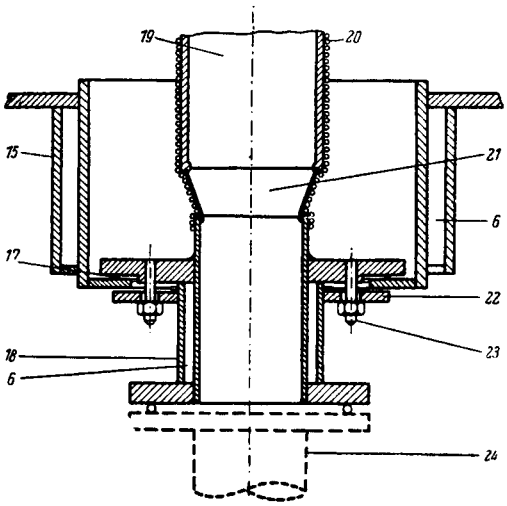


Fig. B 10-247 Design of evacuable hood furnace for simultaneous annealing and degassing of large transmitter tubes at elevated temperatures

1 evacuable furnace space; *2* annular air-cooling flue; *3* furnace lagging; *4* distance pieces for flue walls; *5* upper steel sealing flange; *6* water-cooling channel; *7* water-cooled pumping tube for evacuating furnace *1*; *8* baseplate; *9* support members; *10* lower steel sealing flange; *11* water-cooled lead-through for thermel; *12* wire cable to support hood; *13* adjustable coverplate for flue *2*; *14* electric heater; *15* lead-through tube for pumping stem of transmitter tube; *16* water-cooled connector between baseplate *8* and lower flange *10*; *17* rubber O-ring; *18* water-cooling jacket for tube pump-stem; *19* glass connexion tube to transmitter tube; *20* asbestos wrapping cord to assist thermal equilibrium between hot glass and water-cooled pumping stem; *21* Cu or Kovar ring for sealing to glass; *22* two-section annular compression flange for bolting part *1* to part *15*; *23* clamping bolts; *24* pump connexion with flange and O-ring seal (rubber)

given off in decomposition of the hot glass can be kept small by carrying out the seal-off as quickly as possible. To achieve rapid collapse of the sealing zone without incurring the danger of a blow-in due to atmospheric pressure, the stem at the seal zone of large

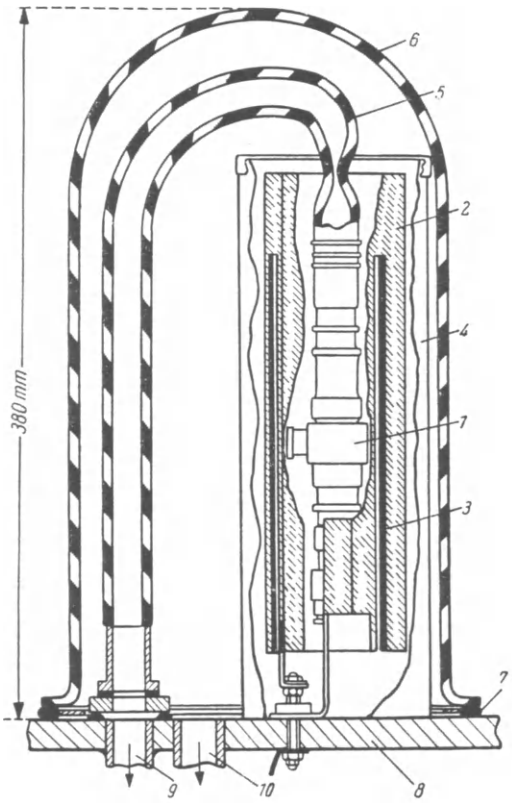
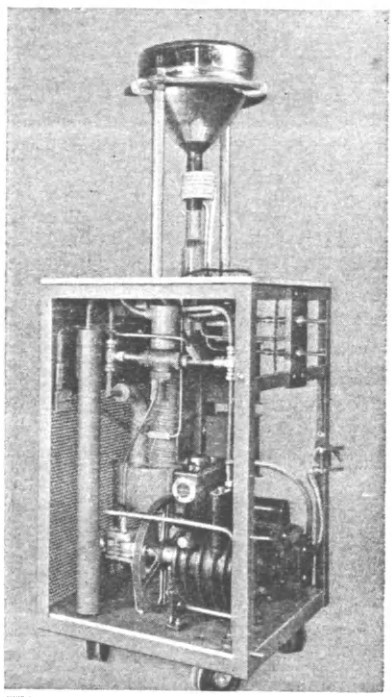


Fig. B 10-247A Design of an evacuable hood furnace for high-temperature degassing of small USW tubes, especially those with Mo ring seals to hard glass (HILLIER)

1 hard-glass tube to be degassed; *2* furnace for degassing temperatures above 700°; *3* self-supporting heater, wave-wound from cut Mo strip 0.25 mm thick; *4* Ni sheet radiation screens; *5* pumping line to tube; *6* hard-glass evacuable bell-jar; *7* rubber O-ring seal; *8* cooled metal baseplate; *9* connexion to oil-diffusion pump, 10^{-7} ultimate; *10* pumping line to auxiliary diffusion pump, 10^{-5} Torr ultimate



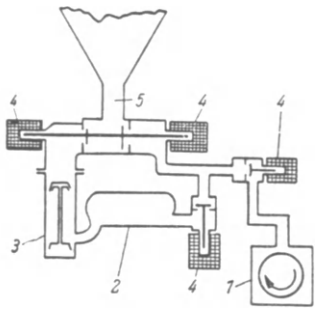
[10.5]

Fig. B 10-248 American-made "trolley" for TV tube production (made by CONSOLIDATED VACUUM CORP., Rochester, N.Y., USA)

tubes should be slightly constricted and if the pumping line is large in diameter the wall should be somewhat thickened here. However, the I.D. should not be too small or the pumping speed will be reduced. To produce a rapid and uniform seal-off, the tube should be drawn off the pumping line as the seal is made (Fig. B 10-252). Drawing off a large tube evenly by hand presents difficulties because of the weight and size of the

tube; the tube is therefore left in position in its frame and, after the seal zone has been softened, the pumping unit is removed on rails provided for the purpose. Figure B 10-253 shows such an arrangement for high-power transmitter tubes. With the trolley shown in Fig. B 10-249, the draw-off is accomplished by a hand-operated lever on the front and to one side, which permits a slow lowering of the HV connexion + diffusion pump, as the connexion between this and the forepump is a flexible metal tube.

[10.5]



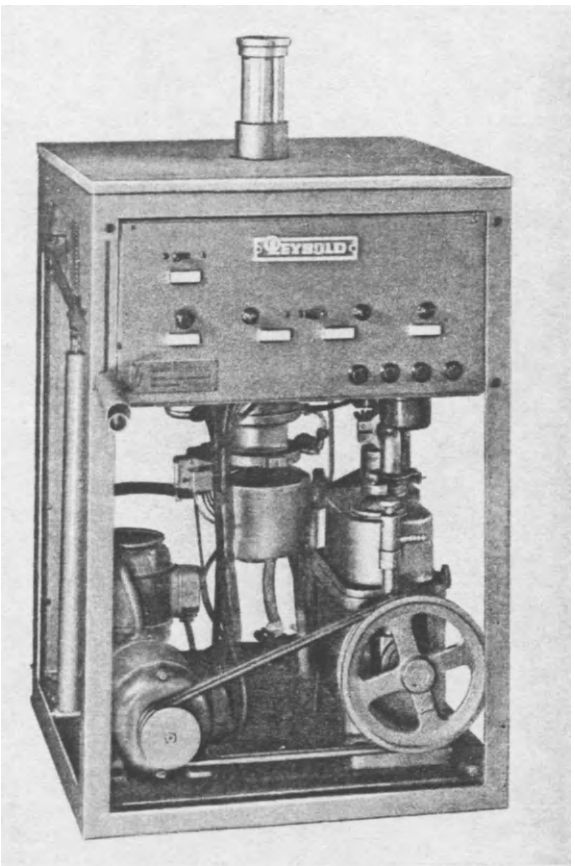


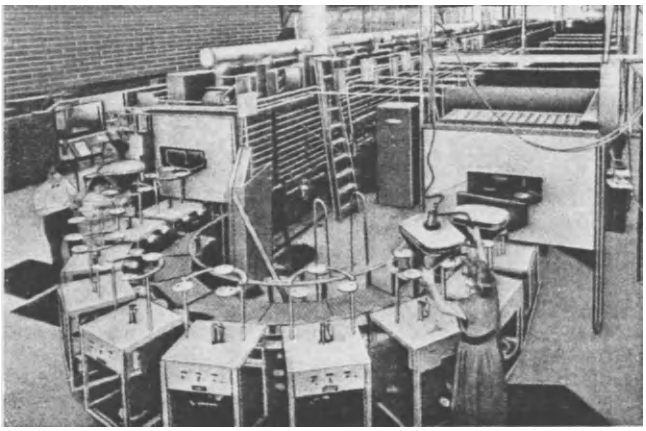
Fig. B 10-249 European make of in-line system trolley (especially for TV tubes) (made by LEYBOLD, Köln-Bayental)

Above: design with valves, *1* forepump; *2* fore-vacuum "storage"; *3* diffusion pump; *4* electromagnetically, mechanically, or pneumatically controlled valves; *5* pump-stem of tube. *Right:* production model without valves (Type P 10): the (upper left front) handle is for lowering the pumping tube and diffusion pump to facilitate seal-off of the fixed-position envelope

However well-conducted the seal-off process is, there is a certain unavoidable rise of pressure in vacuum tubes or contamination of gas-filled tubes due to the gases released by melting the exhaust stem; nevertheless, this gas can be removed by gettering (Chapters 27 and 28) or in the case of HV tubes, by clean-up effect, after seal-off.

See 10.4.V, for removal of gas and water vapor layers on glass to be coated with an adherent metal deposit produced by sputtering or HV evaporation; the removal is carried out by ion or electron bombardment (glow discharge or electron "brush-off").

All personnel concerned with pumping and transport of large glass devices such as TV tubes, transmitting tubes, X-ray tubes and Hg-glass rectifiers, are exposed to im-



[10.5]

Fig. B 10-250 Covered in-line system (trolley-way) for large TV picture tubes (courtesy of RAYTHEON MFG. CO., USA)

Right: loading, and entry tol arge glass degassing furnace

Left: (3 m before exit); H.F. degassing, generators clearly visible between outward and return runway. In foreground six blank stations for cooling down the pumps before air-inlet and reloading. The tubes are heavy and are held during loading by a suction mask on the screen panel

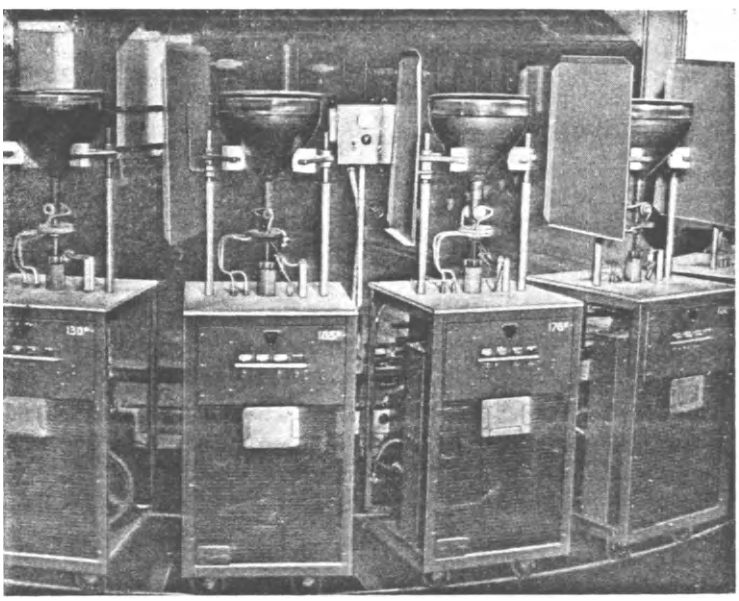
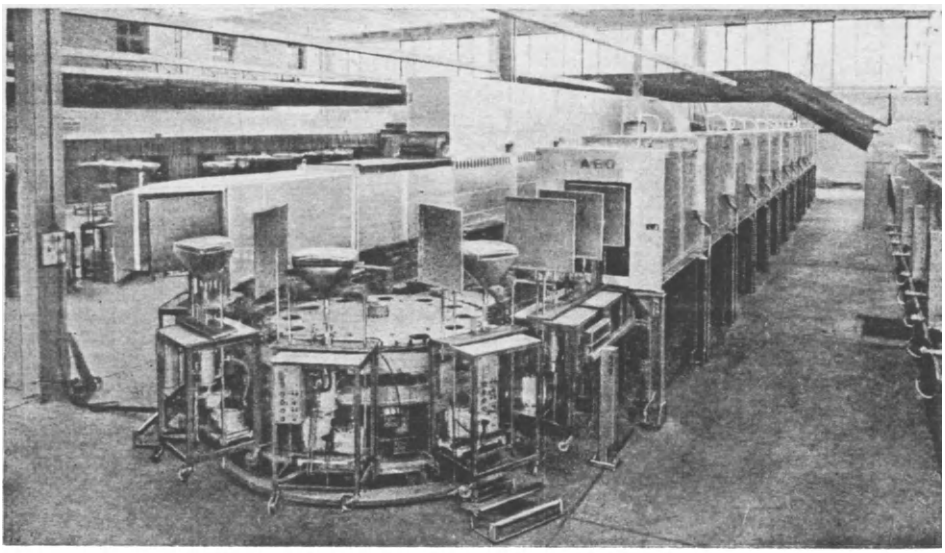


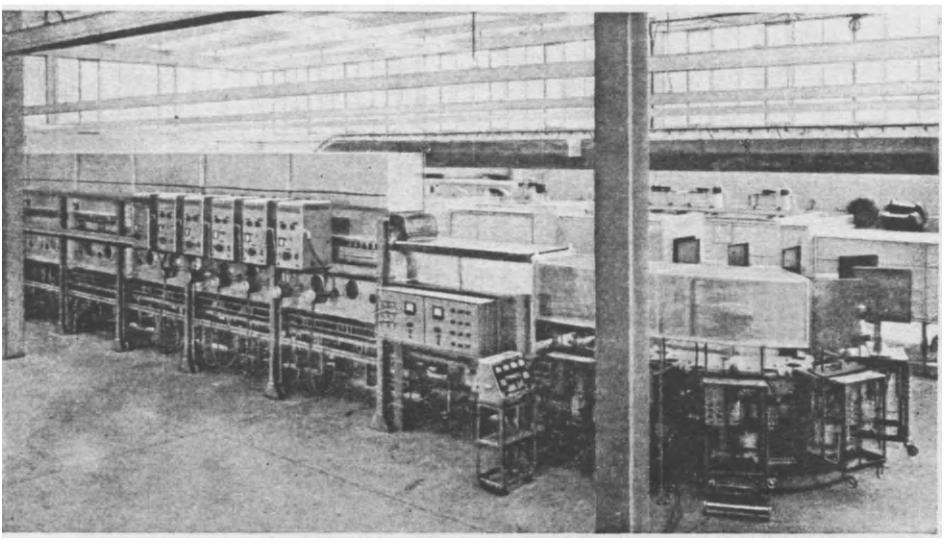
Fig. B 10-250A In-line system for large picture tubes (whole plant made by CONSOLIDATED VACUUM CORP., Rochester, N.Y., USA)

On each trolley near the tube a large metal screen is placed to protect neighboring tubes from impolsion of any one tube. H.F. generators (made by SCIENTIFIC ELECTRIC, Garfield, N. J., USA) are clearly visible in the center of the oval runway

[10.5]



I



II

Fig. B 10-250 B European construction of in-line system for picture tubes with 84 trolleys 65 cm apart (courtesy of TELEFUNKEN-RÖHRENFABRIK, Ulm)

I side view of 20 m degassing furnace
II view of the side with six independent H.F. generators for degassing

plosion hazard; they should therefore always wear safety glasses or the generally more comfortable face-masks of curved Plexiglass (Lucite, Perspex) which do not restrict the field of view.

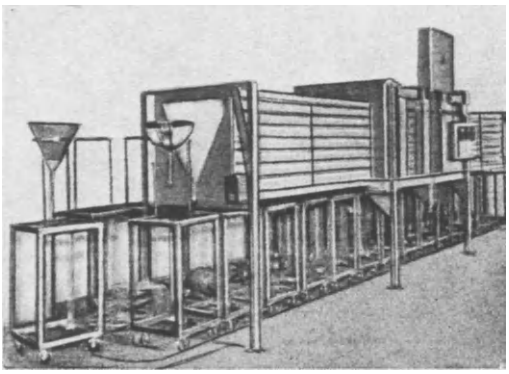


Fig. B 10-251 8 m glass degassing or annealing oven, electrically heated, for large TV tube in-line pumping system (made by EISLER ENG. Co., Newark, N.J., USA) Type 65-SIE. Cf. also Fig. B 10-178. Pre-heat, heating and cooling zones are each 2.4 m long

Fig. B 10-252 Drawing-off the completed tube by hand (cf. also WOYTACEK)

[10.5]

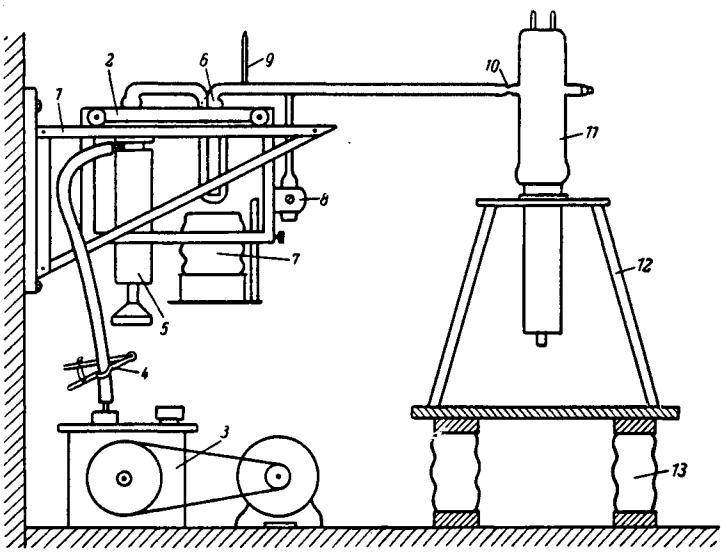


Fig. B 10-253 Sealing off a large transmitter tube by withdrawal of the whole pumping unit once the exhaust stem sealing zone has been properly degassed and softened by gas torch

1 bracket; *2* trolley on rollers with HV pumping unit; *3* rotary oil pump; *4* closure clamp for backing line; *5* Hg diffusion pump; *6* cold trap; *7* Dewar flask + liquid air; *8* vacuum gauge, PENNING type + magnet; *9* side-arm for blowing in air when making the seal-off zone *10*, and which can be cracked off at the tip for air inlet during the air-bake (Table T 9.2–8, No. 6); *11* transmitting tube on pumping stand; *12* legs; *13* stand insulators

10.6 Glass Powder

The use of glass powder as a fabrication material has recently become very widespread in vacuum technology, in the manufacture of (I) glass solder, (II) enamels, and (III) sinter glass moldings.

10.6.I. *Solder Glass*

([3, 4]DALE, DALTON, DENTON, [11]ESPE, [2]GALLUP, GROSS, [4]KNAPP, ZINKE)

[10.6] The term means quite generally glasses used to join a glass body to others of glass, metal or mica. The softening point, like that of metal solders, is sufficiently below the softening or melting point of the partners to be joined that the latter do not soften, deform or deteriorate during the soldering process. This is in contrast to intermediate glasses (see 10.2.II) which are analogous to the filler metals of welding.

(a) *Requirements.* A technical solder glass must fulfil the following demands which makes development of these solders difficult since it is not simple to meet them all simultaneously:

1. The solder must have a composition which ensures a reliable glassy state after melting down the components; it should therefore have the least possible tendency to devitrify (crystallize) even under prolonged heating at the soldering temperature or below.
2. Softening and transformation temperature (see 10.2.II) must lie between 300° and 400° for soldering ordinary silicate glasses so that one can work with soldering temperatures between 400° and 550°, i.e. low enough to avoid softening the workpieces. For soldering mica windows to metal flanges, the soldering temperature can be somewhat higher because of the relatively high calcination point of mica. The viscosity of the solder must be about 10^4 to 10^6 P at temperature, to ensure sufficient but not excessive flow over the joint; the viscosity of the partners joined must be at least 10^{13} to 10^{12} to avoid with certainty any deformation during the process. (10^{13} to 10^{12} P is the deformation range, depending on dimensions, particularly wall thickness. Roughly, one can work at an upper limit of 30–40° above annealing point.) An example here is the use of CORNING solder glass 7570 for joining CORNING magnesia glass 0080 partners; the difference in softening temperatures of the partners and the solder is 696 − 440 = 256° (see Fig. B 10-259B and Table T 10–4, A1).
3. The mean expansion coefficient of the solder glass between room and transformation temperatures must—apart from exceptional cases—be a good match to the partners (e.g. glasses) to be joined.
4. As with metal solders, there must be mutual bonding; chemical bond, solution, or ion exchange. (This is not only for reasons of "form-lock" or fit.) The solder glass must, in other words, wet the joint properly if it is to be vacuum-tight and strong. Where metals must be joined to glass or enamel, the solubility of the thin adherent surface layers of metal oxide in the glass plays, as is well known, a predominant role in the production of vacuum-tight joints; Chapter 30 gives more detail on this.
5. The solder must be inert to the atmosphere in which the joint is used; for example, it must not be attacked or dissolved by water and CO_2 in the ordinary atmosphere. These points do not apply to joints that operate in vacuum, as where fluorescent

powders are bonded to the inner wall of vacuum tubes, or joints between electrodes and their ceramic supports in vacuum tubes. However, glass solders must not decompose at the operating temperature of the tube, and above all must not continuously outgas.

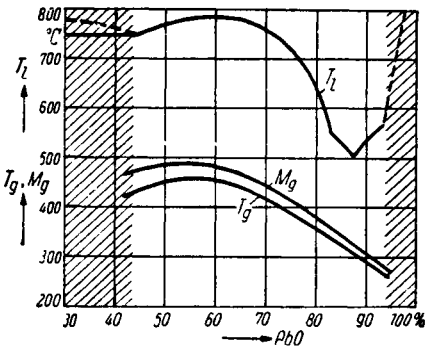


Fig. B 10-254 Transformation temperature T_g, softening point M_g and liquidus temperature T_l of lead-borate glasses, as functions of their PbO content (w/o). Curves for T_g and M_g from KLEMM, T_l from [2]MANNERS. The devitrification ranges are hatched

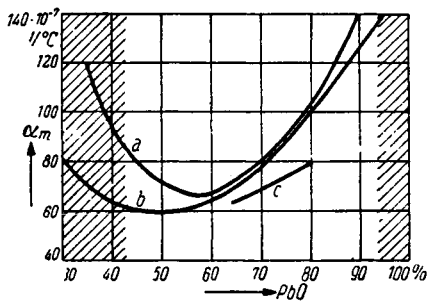


Fig. B 10-255 Mean thermal expansion coefficient α_m (20° transition temperature) of lead-borate glasses as functions of their PbO content (curve *a* from [2]MANNERS, *b* from KLEMM, *c* from [3]DALE)

[10.6]

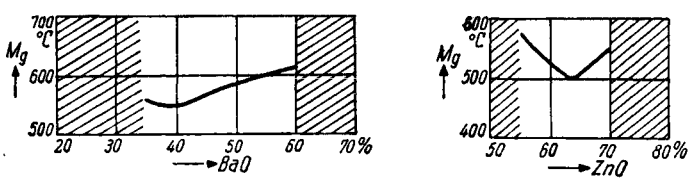


Fig. B 10-256 Softening point M_g of barium and zinc borate glasses as functions of BaO and ZnO content ([3]DALE)

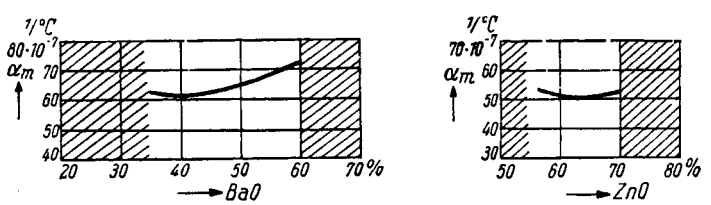


Fig. B 10-257 Mean thermal expansion coefficient α_m (20° transition temperature) of barium and of zinc borate glasses as functions of BaO and ZnO content ([3]DALE)

(b) *Composition and manufacture of solder glass.* Experience to date has shown that the stated conditions are best met by borate-based glasses. For example, the glassy range of binary lead-borate glasses extends over 44–93% by weight of PbO, and the

most suitable range with lowest devitrification tendency lies between 70% and 85%. The softening point here lies between 440° and 350° (Fig. B 10-254) which is far enough below that of most technical glasses, in fact below their transition temperature. Fortunately the αs lie between 80 and 120×10^{-7} l/°C (Fig. B 10-255), a sufficiently good match to soft silicate glasses. Unfortunately, these glasses are not chemically resistant.

Other binary borates, such as those of Zn or Ba, have a relatively high softening point (550–610°, 500–580°, see Fig. B 10-256) and are only suited to hard glasses, and then only for those of α between 50 and 70×10^{-7} (see Fig. B 10-257). It was discovered
[10.6] that weathering resistance of the lead borates could be much improved by adding small amounts of other oxides like ZnO and BaO, without intolerable alteration in the softening point or expansion coefficient, and during World War II TELEFUNKEN (DÜSING) and later English glass manufacturers ([4]DALE, [2]MANNERS) developed a whole series of glass solders. These were in essence lead borate with ZnO or Al_2O_3 additions + a small amount of SiO_2. Table T 10–34 gives details of composition (so far as they have been publicized) and the most important properties.

Glass solders are generally made by careful weighing and comminuting the individual components, mixing well, and then melting down for several hours in Pt crucibles because the lead borates are highly corrosive. The GENERAL ELECTRIC Co., in Wembley, has successfully used Ag crucibles but it was observed that small amounts of Ag cations go into solution in the melt and colour it a light pink. When the melt is homogeneous, it is cast into cold water where it solidifies and breaks into irregular pieces, or granules. For making glass solder paste, these granules are milled in a ball-mill with water and small quantities of ammonia or lithium chloride as deflocculants, until a viscous paste forms. The grains may be ball-milled dry with alumina or flint balls for 8–10 hr until powdered. Oversize particles are sieved out by 100 mesh sieve (see 9.5–13A, Vol. 1) and undersizings are removed by sieving through 200 mesh. The powder is then stirred in distilled water to a brushing consistency, or is suspended in a solution of amyl acetate + nitrocellulose.

Obviously, fused solder glass can be cast to thin rods like the metal rods used for torch brazing. For the same purpose, solder glass can be poured into Ag tubes with an opening and heated by a coil to the point where solder glass flows from the opening as from a fountain pen and over the joint it touches.

(c) *Properties of solder glasses and their measurement.* The main properties are transition temperature, softening point, and expansion coefficient. They are measured in a dilatometer as for glasses, using small cast rods about 5 cm long and 3–5 mm dia. (10.2.IV). The very soft borate glasses need longer to anneal than silicate glasses of the normal type. This is no disadvantage in soldering because only a thin layer of glass remains in the joint so that no large stresses or strains can arise. This property has to be taken into account in expansion measurements by good tempering and very slow cooling if reliable characteristics are to be drawn. Curve *a* in Fig. B 10-258 shows measurements on an untempered borate glass rod and resembles that of untempered silicate glasses (Fig. B 10-22B). Curve *b*, however, was measured on a rod of the same glass tempered for $^1/_4$ hr at 450° (i.e. above the transition temperature) and the cooling rate was 2°/min, the usual one for a silicate glass; this curve drops off near the transition temperature which is not typical of a silicate glass. One can only produce a characteristic

TABLE T 10–34. COMPOSITION AND PROPERTIES OF SOME COMMERCIAL SOLDER GLASSES

MFR.	NAME OF SOLDER	COMPOSITION PbO (%)	B_2O_3 (%)	ZnO (%)	Al_2O_3 (%)	SiO_2 (%)	Na_2O (%)	EXPANSION COEFFICIENT (1/°C)	SOFTENING TEMP. (°C)	SOLDERING TEMP. (°C)
BRIT. THOMSON-HOUSTON CO.	Soft solder glass	70	x	x	?	>5	?	83×10^{-7}	410	>500
	PZS 2	63.77	14.66	16.57	—	≈5.9	—	76.5×10^{-7}[3]	415[1]	550
	P 2	79.4	20.6	—	—	0.3	—	95×10^{-7}	—	370
	PZ 7	72.5	21.5	—	—	6.3	7.0	86×10^{-7}	—	380
	PZ 13	71.5	12.5	—	—	0.9	15.0	92×10^{-7}	—	380
CORNING	Experimental solder, DALTON	75	11	—	11	3	—	83×10^{-7}	440[9]	—
		72	18	5	2.5	2.5	—	83×10^{-7}	428[9]	—
		67.5	14	15	2.5	2.5	—	81.3×10^{-7}	414[9]	—
		68.4	12.4	17.5	—	1.8	—	82.3×10^{-7}	402[9]	—
	Solder glass 7570	Composition unknown						84×10^{-7}[11]	440[10]	—
FISCHER, Ilmenau	F 3	73.8	11.2	—	0.2	14.3	0.5	90×10^{-7}	≈400	≦540
GEN. EL. CO., Wembley	G SS 38	80	20	2.5	—	—	—	96×10^{-7}	300	475
	G SS 34	70	30	2.5	—	—	—	80×10^{-7}	360	525
	G SS 1	84	16	8.0	—	2.0	—	92×10^{-7}	325	500
PHILIPS[7]		80	16	4				96×10^{-7}	420	
SCHOTT UND GEN., Mainz	8435 8461 8468	see Table T 10–4, D 9								
TELEFUNKEN	Soft glass solder T 209	78	14.8	—	1	5	1.2	90×10^{-7}[4]	365	410
	Soft solder glass VUS[5]	77.2	12.1	7.8	—	2.9		91×10^{-7}[6]	340	
	Hard solder glass[8]	30	59	3	1	7	—	$50\text{–}60 \times 10^{-7}$	—	650–700
		35	50	3	—	10	P_2O_5: 2			
		38	45	1	1	15	—			
VERRERIES DE BAGNEAUX	M 129	Composition unknown, apparently silicate enamels						90×10^{-7}	420[1]	(620)[2]
	M 130							111×10^{-7} [12]	360[1]	(560)[2]
	G 50								354	550
VEB WEISSWASSER	Solder glass	73.0	20.4			6.6		78×10^{-7}		500
VÚS, Hradec Králové (ČSR) [14]	7908	80.0	16.0	4.0	—	—	—	90.8×10^{-7}	360[13]	—
	7909	76.0	20.0	4.0	—	—	—	81.1×10^{-7}	400[13]	—
	7941	79.5	12.5	8.0	—	—	—	95.3×10^{-7}	318[13]	—
	7966	72.5	17.5	10.0	—	—	—	81.4×10^{-7}	340[13]	—
	7980	72.2	12.1	7.8	—	2.9	—	90.8×10^{-7}	340[13]	—
	8009	78.6	11.9	4.8	—	4.8	—	86.4×10^{-7}	365[13]	—
	8083	85.0	7.5	—	—	—	—	101.8×10^{-7}	225[13]	—

[10.6]

like that of a well-tempered silicate (curve *c*) if, after the 450°, 15 min tempering, the cooling rate from 450° to 300° is only $^1/_2$°/min and 2°/min below 300°. Figure B 10-29 shows the curve for a tempered silicate glass, and it is typical that the knee inflects upwards at the transition temperature. Curve 1 of Fig. B 10-259 shows a good char-

[10.6]

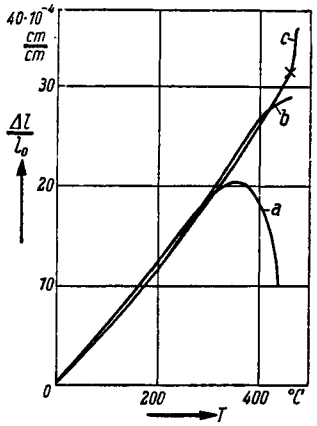


Fig. B 10-258 Relative thermal expansion $\Delta l/l_0$ as temperature (T) function, of a borate glass rod after heat-treatment of various kinds ([3]DALE)

a not tempered; *b* tempered at 450°, then cooled at 2°/min; *c* tempered at 450°, then cooled at 0.5°/min between 450° and 300°, then at 2°/min below 300°

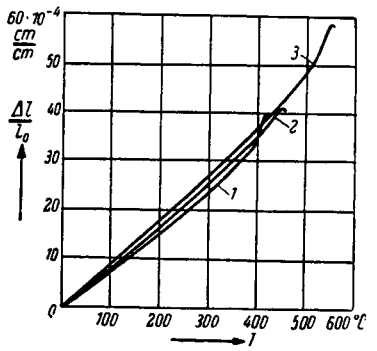


Fig. B 10-259 Expansion characteristic of a soft solder glass (*1*) made by BRITISH THOMSON-HOUSTON CO. LTD., compared with foot-glass C 12 (*2*) and bulb-glass C 19 (*3*) by the same firm ([3]DALE)

acteristic for a commercial borate glass made by BRITISH THOMSON-HOUSTON CO. LTD., compared with their foot-glass C 12 and bulb-glass C 19. Figure B 10-259A shows similar curves for CORNING solder glass 7570 compared with their lamp-bulb glass

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Footnotes to Table T 10-34

(1) Transition temp.: softening temp. apparently 25–35° higher.
(2) Estimated.
(3) Between 0° and 200 °C.
(4) At 0 °C 88.2×10^{-7} 1/°C
100 °C 94.6×10^{-7} 1/°C
200 °C 103.0×10^{-7} 1/°C
300 °C 107.7×10^{-7} 1/°C
365 °C 112.9×10^{-7} 1/°C
(5) Experimental glass.
(6) Between 20° and 50 °C.
(7) KRATOCHVÍL.
(8) From ZINKE, matches Osram glasses 362a and 637a.
(9) Softening point ($\eta = 10^{7.6}$ P).
(10) Determined from the viscosity curve Fig. B 10-259B.
(11) Cf. also Fig. B 10-259A. See C. P. SMITH on a CORNING solder glass with $\alpha = 96.5 \pm 0.5 \times 10^{-7}$ 1/°C.
(12) Suitable for vacuum-tight joints between mica disks and glass flanges (see Chapter 13).
(13) Determined from dilatometer curves.
(14) [1]SLOSIAR.

(magnesia lime soda) 0080. Obviously, the softening point of a solder glass can also be found from measurements of the overall viscosity curve (e.g. by set-ups of the type shown in Figs. B 10-9 and B 10-14). Figure B 10-259B shows the viscosity curve of CORNING 7570 compared with their bulb-glass 0080.

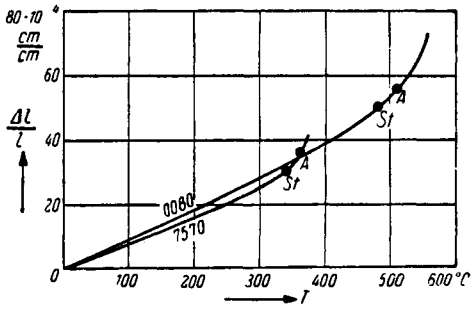


Fig. B 10-259A Expansion characteristic of Corning solder glass 7570 compared with Corning magnesia bulb-glass 0080 (DALTON)

St = strain point; *A* = annealing point

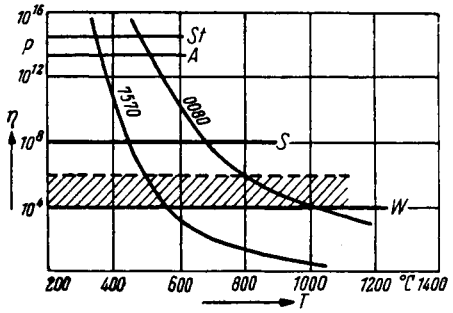


Fig. B 10-259B Viscosity η of Corning solder glass 7570 compared with their magnesia bulb-glass 0080, as temperature functions (DALTON)

St = strain point; *A* = annealing point; *S* = softening point; *W* = working point; hatched region = preferred range of η for soldering

[10.6]

With regard to the wetting ability mentioned above, the borate glasses are specially efficient because of their high chemical reactivity. Wetting can be tested as follows: the glass, metal or mica work-piece is a flat, laid horizontally. On this a cylindrical rod of the solder glass under test is placed. The assembly is put in a furnace and held at soldering temperature; the time-dependent variation in contact angle φ between solder

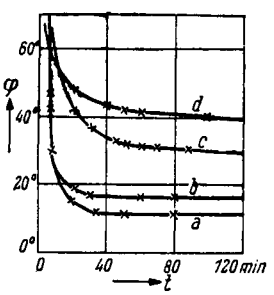


Fig. B 10-260 Contact angle φ on various work-pieces (*a*–*d*) of a lead-zinc borate glass when heated at 440° (constant), as a function of time *t* (³DALE)

a Cu; *b* silver-plated Fe; *c* natural mica; *d* alkali-lime silicate glass (almost the same curve holds for alkali lead-silicate glass)

glass rod and the flat is measured by optical means in the direction of the rod axis. Figure B 10-260 gives results of such measurements on a lead-borate glass with Zn addition. φ drops after a while to a constant value which is lowest for Cu (curve *a*), since Cu is very well wetted by all glasses due to the high solubility of CuO in glass. Alkali lead silicate (foot-glass) and lime-alkali silicate glass (bulb-glass) are reliably wetted also (curve *d*). The wetability of mica lies between that of Cu and of silicate glasses (curve *c*). To increase the wetting of solder glass, the recommended procedure

with many metals is to give them a thin coating of Cu, Ag, Cr or Ni; this too is in agreement with the empirical fact that the oxides of these metals in particular dissolve very readily in glass. Curve *b* in the figure shows that silver-plated Fe quickly develops a relatively small contact angle, a sign of good wetting.

A further fitness-for-purpose test for solder glass is as follows: a plate of the glass to be soldered is covered with the solder glass, in the form of dry powder comminuted in an agate mortar, placed in a muffle furnace and heated to the point where the base

[10.6]

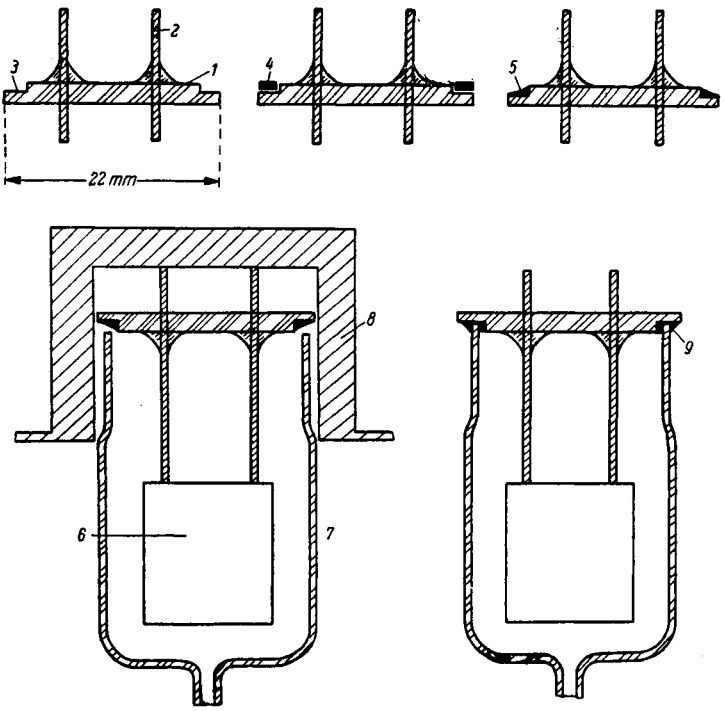


Fig. B 10-261 Method of manufacture of a solder glass joint between press-foot and envelope of miniature tube; soldering temperature *ca.* 450°

1 press; *2* seal wires; *3* shoulder for solder glass; *4* solder glass ring before melting; *5* solder glass after melting; *6* electrode mount; *7* envelope; *8* metal cap; *9* completed joint

glass just does not deform. The solder glass is suitable for this base glass if it fuses properly to the base but shows no sign of devitrification after $^1/_2$ hr at the given temperature.

(d) *Applications of solder glasses.* There is a whole series of possible applications in vacuum technology of which the following appear particularly worth mentioning:

1. *Soldering presses or dished bases to magnesia-glass envelopes of small radio tubes.* This process is of great importance for making tubes with thermally sensitive internal components. Figure B 10-261 illustrates how it is done; the solder glass powder is pressed into a ring with nitrocellulose as binder. The press is then heated in an elec-

trical conveyor furnace to the M.P. of the solder and the binder is completely burned off. When the solder ring (5) has fused to the sealing rim, the foot has cooled slowly and the electrode mount has been assembled (6), the press-foot and mount are laid on to the edge of the envelope neck (7). The envelope is placed stem downwards on a glass-soldering turntable (Fig. B 10-262). A metal cap (8) is dropped over the joint and its immediate surroundings to protect the joint and possibly the internal parts from direct effects of the flame, to exert a light pressure on the joint, and above all to produce homogeneous heating and *slow* rise and fall of temperature of the whole foot without rotating the tube during the soldering process. The tubes now turn with [10.6] the table and pass through a gap between two lines of batswing flames radial to the metal cap (Fig. B 10-262). When softening point of the solder glass is reached, the

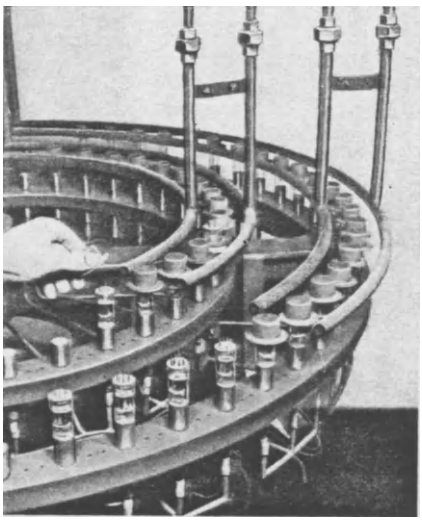


Fig. B 10-262 Turntable machine for bulb-sealing (foot to envelope) under protective gas as per Fig. B 10-261 (courtesy of PHILIPS)

edge of the envelope is forced into the solder mainly under the weight of the cap (No. 9, Fig. B 10-261); after cooling and setting, a strong, vacuum-tight seam is formed, for which about 100 μ of solder thickness between foot and envelope is enough. If a solder glass is chosen whose working temperature is at most 450°, the electrode system and particularly the sensitive cathode of a small tube only 22 mm dia. will not exceed 230°. With ordinary sealing technique (Fig. B 10-139), it would hardly be possible to avoid short excursions to 500–600° cathode temperature in the same size tube (ALMA). Clearly, N_2 can be introduced through the pumping stem at slight excess pressure to act as a protective gas during heating, just as in bulb-sealing. Soldering and evacuation of tubes on the same automatic machines can be successfully carried out in sequence or even overlap without having to cool the foot between the two operations. It is recommended that the expansion coefficient of the envelope glass in which the press in *inserted* be somewhat larger than that of the press so that the joint is under slight *compression* after cooling. C 19 and C 12 (Fig. B 10-259) are suited to each other and to the solder glass from this viewpoint.

Soldering the press in this way also has the advantage that, because the working temperature is low, both press and envelope keep their dimensions exactly without distortion. Previously forming a lug in the glass (Fig. B 10-262A) is a simple way of ensuring correct location in the socket. If the tube is cemented into a base or screening ring, the joint can be closer to the pins than is possible with presses that have been fused into the envelope.

[10.6]

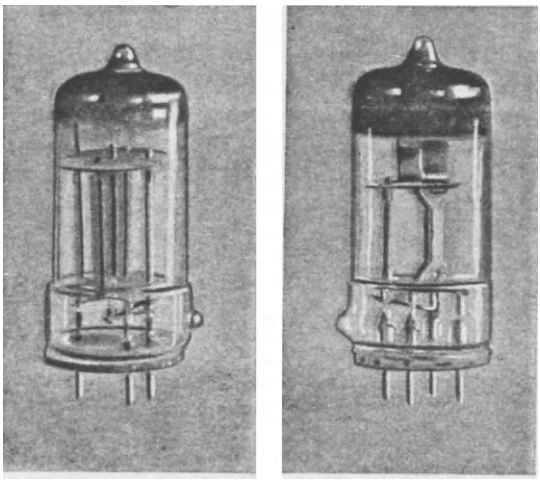


Fig. B 10-262A Tubes with press (22 mm dia.) sealed in by solder glass, locating lug formed on the neck of the tube (courtesy of PHILIPS)

Left: TV diode, V_{max} 8 kV approx.; *right:* double diode for USW reception [ALMA]

Solder glass has been successfully used in the process developed by the COMP. GEN. DE TEL. SANS FILS (BLEUZE): here, glass parts are provided with optically polished sealing surfaces, pressed together and heated for some time below the softening point to make a vacuum-tight joint (Fig. B 10-139B). Before polishing, the surfaces are coated with a thin layer of relatively low-melting solder glass, or solder paste or powder is placed in a groove at the end of the mating surfaces (Fig. B 10-263).

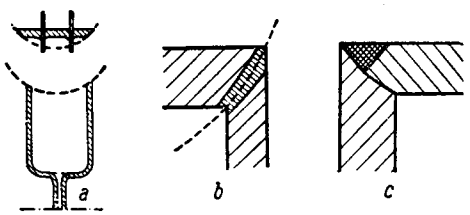


Fig. B 10-263 Process for vacuum-tight soldering of optically polished glass surfaces

a work-pieces, envelope and press, after making the polished mating surfaces for sealing; *b* after soldering with solder glass fused to the surfaces before polishing; *c* after soldering with solder glass applied as paste or powder to a groove along the joint before heating

The mated surfaces can then be heated locally by radiation from a closely placed graphite ring itself heated by H.F., or by a D.H. stainless-steel ring, the whole unit being inside the actual degassing furnace (Fig. B 10-139B). A vacuum-tight joint can be completed in less than 30 sec. The whole tube is then degassed by external furnace.

2. *Soldering front panels of TV tubes and CROs or plane-parallel-ground glass windows of phototubes.* Aqueous solder paste is painted thinly on the soldering surfaces which

should be as flat as possible. The work-pieces are then lightly pressed together, possibly just by their own weight, placed in an electric furnace and slowly brought to softening temperature, then slowly cooled. Surface unevenness of both parts should not exceed 50 μ if possible, and the solder thickness should not exceed 100 μ. In the following section a process is described for soldering glass windows to glass or metal tube flanges.

3. *Soldering of mica windows.* Geiger counters are often provided with mica windows to offer the least possible obstacle to entry of particles or beams to the counting volume (see Chapter 13). These windows can be sealed vacuum-tight to tube flanges [10.6]

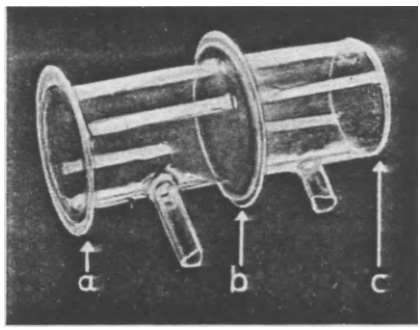
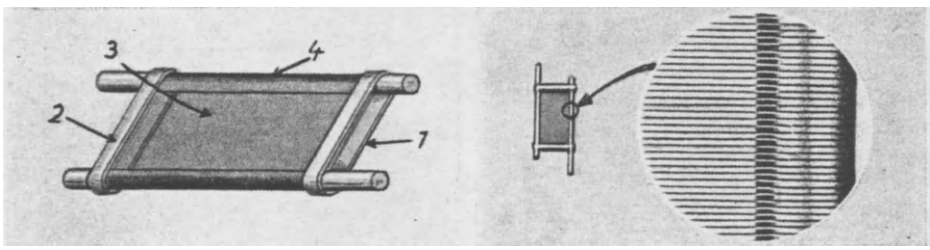


Fig. B 10-264 Vacuum-tight solder glass joints between a lime magnesia glass tube (C19, made by BRITISH THOMSON-HOUSTON CO. LTD.) and a mica disk (*a*), a NiCrFe disk (*b*), and a plane-parallel ground glass disk (*c*) ([3]DALE); cf. also Fig. B 13-19, III



I II

Fig. B 10-265 Attaching very fine grid wires to a frame with solder glass (WALSH)

I grid for a wide-band amplifier tube Type 437A (WESTERN ELECTRIC): *1* grid members of 1 mm dia. Mo; *2* Mo strip cross-members; *3* grid of W wire 7.5 μ dia., spacing 60 μ, 160 turns/cm; *4* solder glass for attaching wires to members
II solder glass joint magn. × 15

of glass, metal or ceramic (ANTON) by means of solder glass, provided that the counter body flange has expansion characteristics that match mica (*ca.* 100×10^{-7} 1/°C, see Chapter 13. Refer to Fig. B 13-6.) Cu-plated nickel iron (50–52% Ni) has proved suitable, for example. The simplest procedure is to lay the mica on the metal flange, put a little solder glass powder on the edges of the mica, or apply glass solder paste; then heat the whole device in an electric furnace to 500–600° and, when the metal and mica are properly wetted by the solder glass, cool, not too fast (*ca.* 5°/min). This technique will make vacuum-tight joints between mica windows and soda-lime glass, thin FeNiCr diaphragms and glass tubing, and flat-ground glass windows and glass tubes (Fig. B 10-264). For further details see Chapter 13 (Mica), especially Fig. B 13-19.

4. *Soldering very fine grid wires to support rods.* Figure B 10-265 shows the process for making frame grids with very fine W wire of 7.5 μ or about one-tenth diameter of a human hair. It is difficult to braze wires to the 1 mm dia. Mo rods at the side of the grid frame with Au braze (cf. Fig. B 4.5-2) because when the temperature needed for brazing has been reached (1075°), although the holding time is only 30 seconds, the tensile force exerted by the Mo on the grid wires will be excessive. Success was achieved in "brazing" the grid wires to the frame rods without damage from tension with the aid of a very thin coating of relatively high-melting solder glass, heated to [10.6] only 715° for 15 minutes (WALSH). The glass did not soften in operation nor did it decompose despite the relatively small gap between it and the incandescent cathode.

When solder glass rather than Au solder is used, the grid wires are not automatically gold-coated during the soldering process of Fig. B 4.5-2; grid emission suppression is desirable, however, and the wires should be specially precoated with Au of about 0.5 μ thickness (cf. also 6.5.XI).

10.6.II. *Enamels*

(ANDREWS, FRYŠ, NOVOTNÝ, PETZOLD, STUCKERT, VIELHABER)

This term means suspensions of inorganic glass-forming materials in a suitable fluid. They are mostly applied to metal or glass in relatively thin layers as paste of proper consistency by painting, spraying or dipping, drying and fusing to the substrate to form thin, continuous glazes. Enamels applied to ceramics are usually called glazes, and are treated with ceramics in Chapter 12, since they have generally already been applied during the firing of the ceramic by the supplier, and serve quite different purposes from those described here.

If such glass layers are produced, not from a suspension of glass powder but by melting a layer of glass with a flux to a substrate, or by coil-winding a glass fiber drawn from a softened glass rod, it is better to describe the material as sheathing glass or wrap glass (see Chapter 30).

(a) *Manufacture of enamels.* This process is similar to making solder glass paste. Composition is set by expansion coefficient, chemical behavior of the substrate, and the temperature which the enamel must stand in operation of the tube. Iron parts can be enamelled with the usual commercial grip or ground-coating enamel. The so-called "coating enamel" which is fused on to the primer serves a purely aesthetic purpose, and is generally not used in vacuum work because its pigments are often sources of outgassing. Ground coats for Fe (see, e.g., KING) are generally made from a whole series of glass-formers (quartz, feldspar, borax, fluorspar, soda, calspar, etc.) plus certain auxiliary agents (alkali saltpeter, manganese dioxide) and so-called bonding oxides (cobalt oxide, nickel oxide) which are all finely milled and mixed together. The mix is smelted in conveyor furnace or refractory crucibles at temperatures up to 1300° to a glassy material sometimes called the base, flux or "fondant". The true "fluxes" (borax, fluorspar, etc.) are thus liquefied and react with the "incombustibles" (quartz, calspar, alumina) to form silicates, aluminates, and borates. Smelting is continued until gassing ceases ($1^1/_2$–$2^1/_2$ hr). The hot liquid melt is then quenched in cold water to solidify and fragmentate it. The grains which result (also called "frit") have 35–40 w/o water added (based on weight of dry frit) and are then milled to a creamy consistency in a hard

porcelain mill with porcelain balls. To this mill-batch is added 6–8 w/o of clay (again based on dry weight of frit), either at once or after prolonged milling. This mill-batch additive is to act as a dispersing agent, operating as a negative colloid, which tends to disperse strongly because of its electric charge; the effect is that the fine-ground enamel particles do not settle in the water, but form a "clay suspension". This thick, aqueous suspension adheres evenly to the metal to be enamelled, and the clay after drying also acts as a cement. Milling proceeds usually for 6–8 hours until the particles will pass a 200 mesh sieve (CLAUSER). Experience has shown that the enamel suspension, called "slip", should not be used at once but should be left to age for a few days to ensure that the dissolved-out electrolytes act on the colloids of the suspension. [10.6]

The components of technical enamels are not usually revealed by the works. Table T 10–35 gives the compositions of some enamels.

The following remarks apply to the individual constituents: the chief one, just as in most technical glasses, is silica, SiO_2, mainly as silica sand, but also as clay and feldspar (mostly potash feldspar, $K_2O \cdot Al_2O_3 \cdot 6\,SiO_2$) with some soda feldpar ($Na_2O \cdot Al_2O_3 \cdot 6\,SiO_2$) which also introduces Al_2O_3, K_2O and Na_2O into the enamel. Borax, $Na_2B_4O_7$

TABLE T 10–35. COMPOSITION OF RAW MATERIALS OF SOME GROUND-COATING ENAMELS FOR IRON

MATERIAL	(2)	(1) (3)		(1) (4)		(1) (5)		(1) (6)	
	w/o	w/o	(7) w/o	w/o	(7) w/o	w/o	(7) w/o	w/o	(7) w/o
Quartz	14.4	32	41.1	22.1	28.3	24.7	31.9	20	24.8
Feldspar	36.3	16	20.6	25.5	32.6	22.6	29.2	29	36.0
Borax	35.6	32	41.1	37.4	47.8	34.4	44.5	30	37.3
Fluorspar	5.3	4.5	5.8	3.4	4.3	3.4	4.4	8	9.9
Soda	7.4	9.6	12.3	7.7	9.9	10.9	14.1	7.5	9.3
Calcite	—	—	—	3.4	4.3	—	—	—	—
Alkali saltpeter	—	4.7	6.0	1.7	2.2	3.3	4.3	5	6.2
Pyrolusite	0.65	—	—	—	—	0.6	0.8	1.0	1.2
Cobalt oxide	0.225	1.0	1.2	0.5	0.6	0.3	0.4	0.5	0.6
Nickel oxide	—	0.2	0.3	—	—	—	—	—	—
Total		100	128.4	101.7	130.0	100.2	129.6	101.0	125.3
Mill-batch additives (w/o of dry frit)									
Clay	6	8		6		6		8	
Borax	2.5	1.0		—		—		—	

(1) VIELHABER.
(2) LIDDELL.
(3) For steel apparatus, utensils.
(4) For dishes.
(5) For reflectors.
(6) For signs and stove parts.
(7) Weight units are so chosen that the whole mix gives 100 parts of fused frit (STUCKERT).

$+ 10\,H_2O$, is the main fluxing agent of the enamel industry, and it also serves to introduce Na_2O and above all B_2O_3, which has the property of readily dissolving metal oxides, making the enamel flow well and reducing devitrification. Fluorspar contains 66–95% CaF_2 according to origin, and is added in amounts up to 10% to the enamel where it acts as a flux also. Calcined soda, Na_2CO_3, introduces Na_2O. Calspar (marble flour) introduces CaO. Saltpeter, mostly $NaNO_3$, introduces alkali, but besides that acts mainly as an oxidant to remove organic impurities always present in small amounts in the raw materials. Pyrolusite, mainly as MnO_2, serves the same purpose
[10.6] since when heated it converts to the suboxide, giving off O_2. Thereby it also assists the

TABLE T 10–36. COMPARISON OF UNFUSED GRIP MIXTURE (FOR COATING IRON) WITH MEAN VALUES FROM ANALYSIS OF THE SLIP AFTER SMELTING THE ENAMEL

UNSMELTED MIX (1)		AVERAGES FROM ANALYSIS OF ENAMEL (1)		(2)
RAW MATERIALS	PARTS BY WT.	CONSTITUENT	w/o	w/o
Quartz	27.8	SiO_2	50.5	51
Feldspar	27.7	B_2O_3	15.7	10
Borax	43.8	Al_2O_3	6.5	10
Fluorspar	3.9	Na_2O	14.9 } 19.8	18.5 } 20.5
Soda	8.8	K_2O	4.9 }	2 }
Alkali saltpeter	2.0	CaO	0.6	1.6
Pyrolusite	0.4	CaF_2	5.7	5.0
Cobalt oxide	0.3	bond oxides	1.2	(?)
Nickel oxide	1.0			
Total	127.3(3)	Enamel total	100.0%	98.1%
Mill-batch additives				
Clay	11.3			
Solid constituents of slip, overall	138.6			

(1) STUCKERT.

(2) For comparison, this column gives composition of an Fe-sealing glass RL 16 ($\alpha = 114 \times 10^{-7}$ 1/°C); cf. Table T 10–2, E 3.

(3) Cf. footnote 7 in Table T 10–35.

action of the bonding oxides (see below) and colors the enamel dark. In almost all grips for iron, the bonding oxides are found (Co_2O_3, Ni_2O_3), which have the property of effecting the adherence of enamel to iron (see Chapter 30 for details).

The variable chemical composition of the raw materials in Table T 10–35, mostly naturally occurring minerals, explains why the recipes for making enamels only lead to a defined product if the raw materials are drawn from reliable suppliers and have constant quality, or are subject to continuous quality control by chemical analysis. Also, one has to count on a sublimation loss of 20–30% when smelting the frit mixture and therefore only a terminal analysis of the smelted slip will give a reliable indication of enamel composition. Table T 10–36 gives as an example the composition of an unsmelted base-enamel mixture (left side) while the right side gives average analytical

data on the smelted grip made from the mixture and ready for use. As can be seen, one is in principle dealing, as with most grips for coating Fe, with an alkali borosilicate glass like that of class IV*c* in Table T 10–1, but with a relatively high alkali content. The enamel has also a composition very similar to that of certain Pb-free Fe-sealing glasses, as comparison with the last column of Table T 10–36 shows.

In firms making vacuum components, where ground coating of Fe is necessary, the dry frit is usually drawn from a reliable supplier, stored in sealed porcelain vessels (not metal, to avoid metallic impurities scraped off by the sharp, hard grains), and the slip is made in the works by milling in a hard-porcelain ball-mill; quantities are chosen according to requirements and by recipes proved by the works that supplies the enamel ware. [10.6]

(b) *Enameling.* The surfaces to be coated must be carefully cleaned before the process; oil and grease are removed by hot alkalis, rust by acid pickling or grit-blasting. Enamel is usually applied by dipping. Iron enameling (fusion) is carried out in closed electric chamber kilns in air at temperatures between 760 and 980° (mostly 825–870°) in times up to 1 hour but usually 5–10 minutes. As with ordinary vacuum-tight glass-metal seals, adherence of enamel to substrate can only be achieved if there is O_2 present during the melting process, or with non-ferrous metals, if O_2 has at least the chance of forming an oxide on the metal and penetrating it, before melting.

The enamel thickness is about 100 μ but can be thicker for special purposes. A second enamel layer may be deposited, but in vacuum work this should be a grip coating only. This coating is again fused on. To avoid CO_2 bubbles in the layer, the Fe substrate should contain at most 0.015–0.02% C; other additions: $<0.04\%$ Mn, $<0.010\%$ P, $<0.03\%$ S, Si only traces. Its α–γ transformation temperature should be above 870°, i.e. above the normal melting point of the enamel. The C content of steels and Fe alloys can be higher if stabilized by small amounts of suitable additive, such as 0.3% Ti (CLAUSER). The expansion coefficient selected should preferably be somewhat less than that of the base material so that the layer is never under tension.

(c) *Applications of enamel.* Enamels are used for widely different purposes in vacuum technology:

1. protection of substrate (metal or glass) from corrosion;
2. increased vacuum-tightness of substrate;
3. electrical insulation of metal surfaces;
4. preservation of defined pre-oxidized metal surfaces, and as an intermediate glass for glass-metal seals;
5. special purposes; in contrast to ordinary technology, in vacuum work enamels are not used for coloring or decorative purposes, if one excepts marking dyes with glassy melt-additives which can often be described as enamels (see, e.g., Table T 10–32).

Enameling of Fe and ferrous alloys has proved particularly valuable and the following cases of chief importance should be mentioned:

1. *Water cooled outer surfaces* of Fe envelopes for electron devices (esp. Hg tank rectifiers, ignitrons, Hg-vapor thyratrons) to prevent corrosion and the associated diffusion of atomic hydrogen through the Fe wall (see also 5.3, Vol. 1).

2. *Internal enameling* of such devices at certain zones to prevent onset of arcing or to insulate the cathode pool of a Hg rectifier from the wall of the envelope.
3. *Pre-enameling* of Fe rings for pressed glass to metal seals. (See Fig. B 5.3-9 and Chapter 30.)
4. *Pre-enameling* Kovar, in the form of wire, rod, caps and rings for glass-metal seals of all kinds. A suitable enamel can be made of the glass used for sealing (SCHWARZ-BERGKAMPF). A slip made from pieces of Kovar glass CORNING 7052 or OSRAM 756 b (see Table T 10–2) can be used: the pieces are first ground in an agate mortar to grit [10.6] of about 100 μ sizing, and this is milled to 20–40 μ under methanol + ammonia in a corundum mill with balls of the same material. The slip is then applied thinly by a suitable method (see Chapter 30) to the pre-oxidized regions of the Kovar. The enamel can be fused in H_2 by heating the whole Kovar section by H.F. The enamel melts rapidly and protects the Kovar from reduction at the sealing zone, while the rest of the metal surface is reduced.

   In many cases it is recommended that H.F. melting of the enamel be started with N_2 flushing gas, and only after the enameled metal has cooled to 700–600° should about 30% H_2 be added to the inert gas. This amount of H_2 and the temperatures given are sufficient completely to deoxidize the unenameled parts of the metal, but not to produce appreciable reduction of the seal zone beneath the enamel, which could cause leaks (cf. Chapter 30).
5. *Pre-enameling* sleeves of ferritic CrFe (tubular connecting pins). The best enamel is CrFe sealing glass, $\alpha = 96 \times 10^{-7}$ 1/°C; the material is pounded to make a $^1/_4$ liter grit, in a 2 liter agate mortar, then dry milled for 4–5 hr, sieved through silk 75-mesh sieve, any oversizings remilled and finally the whole mill-batch run through a phosphor-bronze 270 mesh/in. sieve. The sievings are washed *briefly* in distilled water and as soon as the powder has settled and the supernatant has been decanted, dried in an oven at 50° below the softening point of the glass; the sieving is then repeated (25 mesh). Further operations as described above for Kovar enamel.
6. *Enameled lead-throughs*, as specially developed in England for Hg tank rectifiers. Conical and thickly-enameled Fe rings up to 300 mm dia. I.D. are stacked and fused together in an electric furnace to form a tube. See Chapter 30 for details.
7. *Internal enameling* of large-I.D. metal pumping stems which are sealed after the pumping process by hot crimping and are then mechanically cut off; enameling is recommended to increase the vacuum-tightness of the seal (MARTI). Just before cut-off, the stem is heated by current-carrying clamps (see Fig. B 10-266) until the enamel metals and the metal becomes slightly plastic. The stem center is then crimped when still hot between two jaws of thermally insulating material. The solder glass (enamel) forms the final sealing. In the same pass as the crimping, the hot stem is cut off by a combined crimping and forming tool.

Besides these processes for Fe and ferrous alloys, the following applications in vacuum work are worth mentioning:

8. Sheathing thin metal wires with transparent glass coating (vacuum thermels for radiation pyrometry); fine LINDEMANN-glass powder is used for this (see Table

T 10–2A, 1). The wire is dipped in the powder or thinly dusted with it and is then heated to produce an even flow of glass over the surface of the metal. The wire should be installed in the vacuum tube as soon as possible after coating, and the tube evacuated, since LINDEMANN-glass decomposes in the atmosphere.

9. Envelopes and tubes made of ordinary technical glass can be used for lamps filled with Na vapor if, after forming, the inner surface is protected by a Na-resistant enamel from attack by hot, reactive vapor of Na ions. See, e.g., Table T 10–2, D15, E4.
10. See 6.5.IX, Vol. 1 for enameling Dumet, whose surface is oxidized to CuO, with glassy B_2O_3 (so-called "borating"). [10.6]

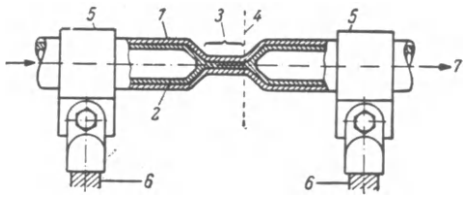


Fig. B 10-266 Seal-off of metal pumping stem internally coated with solder glass (MARTI)

1 steel pumping stem (wall 0.25–0.4 mm, I.D. 13–14 mm); *2* inner coat of solder glass 0.3–0.4 mm thick, *3* crimp area; *4* cut-off zone after crimping (not central but nearer the pump); *5* contact clamps for electrical heating of the stem during seal-off; *6* current leads; *7* to pump

10.6.III. *Vacuum-tight Sinter Glass*

The distinction is made here between sinter glass and multiform glass. The former is made from relatively coarse glass grit of any type, without the aid of suspension fluids or bonding agents, by sintering (fritting) in graphite molds; the molding has a relatively large pore volume. Ceramic glass (multiform) is made of fine powder by methods described in 12.1 for making ceramics; the subject is treated shortly in 10.6.IV below.

"Sinter glass technique" has only been fully developed in recent years ([1,2]DORGELO, [12,13,16]ESPE). The sintered, vacuum-tight bodies primarily facilitate cheap manufacture of hard-glass presses with metal lead-throughs.

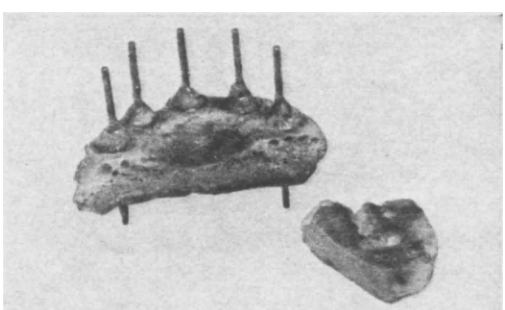
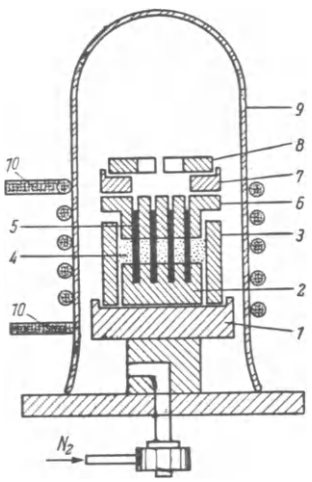
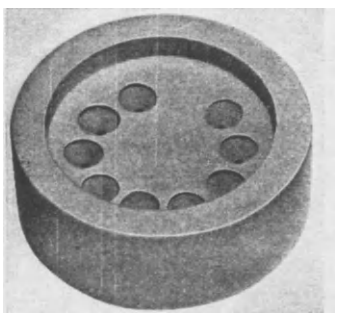


Fig. B 10-266A Portions of presses made by sintering at 1000° water-milled Kovar glass grit; magma-like formation with highly devitrified regions, pores, and whitish precipitates ([13]ESPE)

The starting grit is made by wet-milling, and in contrast to enameling-slip manufacture, the milling fluid (which dissolves substances in operation) is decanted after use, leaving the glass grit. Kovar glasses generally belong to hydrolytic class V because of their high B_2O_3 content; water solubility by the grit method of the DGG (Table T 10–15A) is over 150 mg, whereas it is 5–7 mg for ordinary W or Mo sealing glasses. The leaching

effect of milling water can therefore be so powerful that the grit is unusable; it is scarcely still glass but when sintered has at best the properties of a magma-like porous ceramic (Fig. B 10-266A). In such cases one is forced to pulverize the glass on an anvil with a plunger in an eccentric press, the anvil and plunger preferably of solid glass of the same type as the material to be crushed ([13]ESPE). Another way is to dry-mill in a crusher like a coffee-grinder with hardened steel wheels. Dry-milling in the usual porcelain ball-mill is not recommended as a rule because there is too much take-up of impurities from the walls that are hard to remove. Silicosis is a hazard in making and working with glass
[10.6] grit; face-masks should be worn, work should be carried out under an extractor hood, and dust in the working space should be avoided. Grain size for sinter glass frits is generally between 300 and 700 μ, and up to 1000 μ. On the other hand, there is data from A. HIX stating that the grit was sized by sieving out coarse material





11

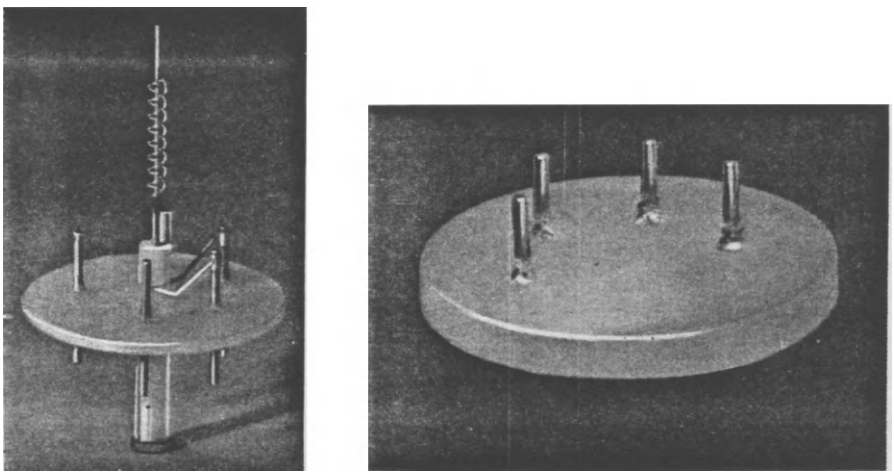
Fig. B 10-267 Manufacture of sinter glass presses ([2]DORGELO, [9]ESPE) (see also Fig. B 10-268)

1 ceramic substrate; *2* lower graphite mold; *3* H.F.-heated graphite ring; *4* glass grit; *5* pre-glassed sealing pins; *6* upper graphite mold; *7* ceramic insulators; *8* slotted Fe ring weight; *9* glass bell, possibly with protective atmosphere (N_2); *10* H.F. work coil; *11* photograph of mold for sinter glass and nine lead pins; *2* and *3* are made of graphite for improved heat exchange

with 400 mesh/cm^2 screening, and the finer material with a 1600 mesh/cm^2 screening, which corresponds to sizings of 150–300 μ.

The sinter glass process itself is explained by Fig. B 10-267. Molds 2 and 11 are electrographite, and should be of dense flawless material made at a high graphitization temperature. This is to ensure smooth, precise surfaces, close tolerances and easy withdrawal of the work-piece after molding, much facilitated by conical fit between mold and molding. Molds should be carefully dried each time at 250° in an oven for 5–8 hr or heated up to 1000° in a dry inert atmosphere two or three times, and used immediately after cooling. In spite of the N_2 atmosphere, graphite in contact with glass loses a little from the surface each time and about $^1/_{10}$ mm is lost in every 20 sintering processes, so a single mold can only be used about 100 times, taking into account the necessary tolerances. The mold is inserted into a graphite tube (3). The lead-throughs are pre-glassed at the seal zone by standard technique (see Chapter 30) with a thin layer of suitable sealing glass. The lead-through metal has about the same α as the glass grit.

The glassed leads are put in the mold and a precise aliquot of glass powder, still hot from drying, is poured evenly between the leads and the surround. The graphite closure (6) loaded with weight (8) and provided with holes for the seal wires is placed over the glass. For glass with maximum grain size of 350–750 μ, the loading of the surface should be 6–10 g/cm^2, and higher if the sizing is smaller. The whole mold is placed under a hard-glass bell-jar (9). Technical purity N_2 is used to fill the bell-jar to 50–90 mm water gauge, and the mold is now heated by external, water-cooled H.F. coil; with presses of 37 mm dia. made from hard glass, 7–9 min is enough, the temperatures being adjusted to produce viscosities of 10^6 to 10^8 P. The grit shrinks in volume (up to 35% for very [10.6]



I II

Fig. B 10-268 Flat presses of sintered hard glass grit

I no exhaust stem, 5 vacuum-tight seals to Mo lead-throughs; after sintering a coaxial double coil of ThW wire is mounted for short-wave tube of the type shown in Fig. B 8.5-24 (made by PHILIPS) (see also [1]DORGELO)
II made of Kovar glass, four Kovar pins

fine grit) and the grains' surfaces melt to form a vacuum-tight but porous body, clouded to some extent by many small gas bubbles; the pins are sealed vacuum-tight in the sinter glass disk at the same time (see Fig. B 10-268). The maximum size of the bubbles is about equal to the grain size of the grit for sinter glass made with times and temperatures given above; most are one-fifth of this size. Presses with grain sizing of 0.5–0.7 mm are still just transparent, while those made from sizings in the range 0.3–0.5 are milky white and opaque. An H.F. generator of 2 kW output power is enough for 37 mm dia. presses made of Kovar glass grit. The N_2 flow should be continuous. The mold should be removed only after cooling to about 250°, and the molding taken from the mold only after cooling to 100–150°. Fairly rapid cooling is permitted.

In practice, mass-production involves either a turntable machine (Fig. B 10-269) or apparatus like that of Fig. B 10-270. In the latter, a simple lift-and-tilt device for supporting several H.F. coils (6 in the figure) permits the first series after sintering to be shifted to the rear to a position where the hot molds can cool during the 10–20 minutes heating-up and sintering process for the next front series. The process is then repeated.

Even relatively small numbers of hard glass presses can be made efficiently by this method, whereas at one time only mass-production glass-molding equipment was economic.

The sintering process can obviously be carried out in ordinary N_2-flushed muffle or conveyor furnaces, but the temperature cycle for the whole operation must be precisely laid down.

By and large, these vacuum-tight sinter glass bodies have the following properties:

[10.6] (a) The smaller the mean grain size of the grit, the larger the pore volume for the same sintering conditions (see Fig. B 10-270A), and the lower the apparent density (Fig. B 10-270B). The shrinkage during sintering is less the smaller the grains.

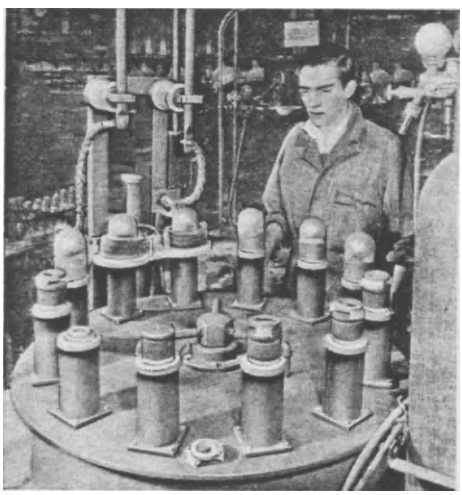


Fig. B 10-269 Turntable for making sinter glass bases with sealed lead pins as per Fig. B 10-268 ([2]DORGELO)

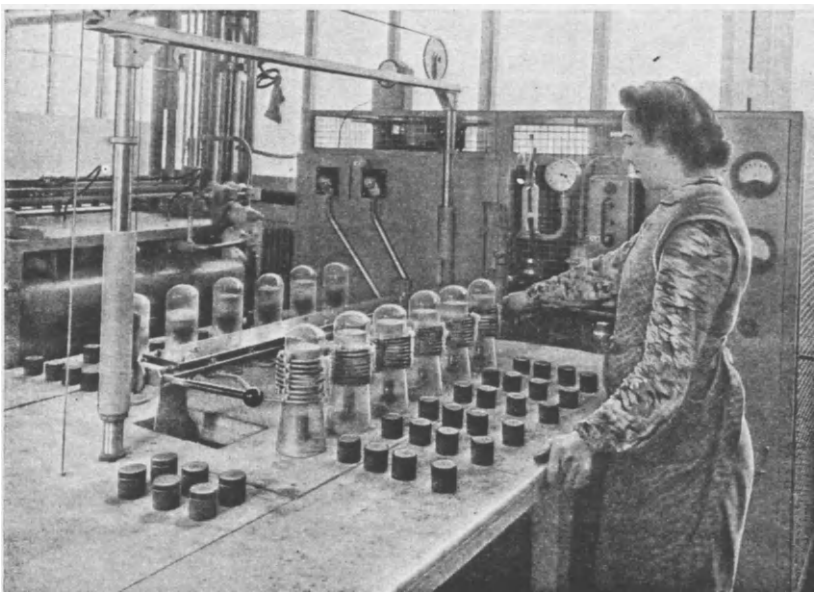
(b) Tensile strengths drop with rise in pore volume; for example, a Kovar glass with 6% pores has 20% less tensile strength than the solid glass.

(c) Thermal expansion between room and transition temperature is the same as that of the bulk glass (Fig. B 10-270C), in agreement with the fact that a hollow body has the same expansion as if it were solid. According to other measurements ([13]ESPE), sintered Kovar glass was found to have a 3–8% higher expansion coefficient than the clear glass, possibly a consequence of changes in composition during comminution and sintering, since Kovar glasses are very sensitive to hydrolysis.

(d) Thermal shock resistance falls slightly with increase in pore volume, apparently less with low expansion glass than with high (Fig. B 10-270D).

(e) Thermal conductivity (corresponding to electrical) is somewhat less than that of the bulk glass (see next section).

(f) The volumetric resistivity rises considerably with porosity (Fig. B 10-270E) and with it the $T_{\varkappa 100}$ value (Fig. B 10-270F). Resistivity follows the RASCH-HINRICHSEN temperature law (see 10.2.X), as Fig. B 10-270G shows.



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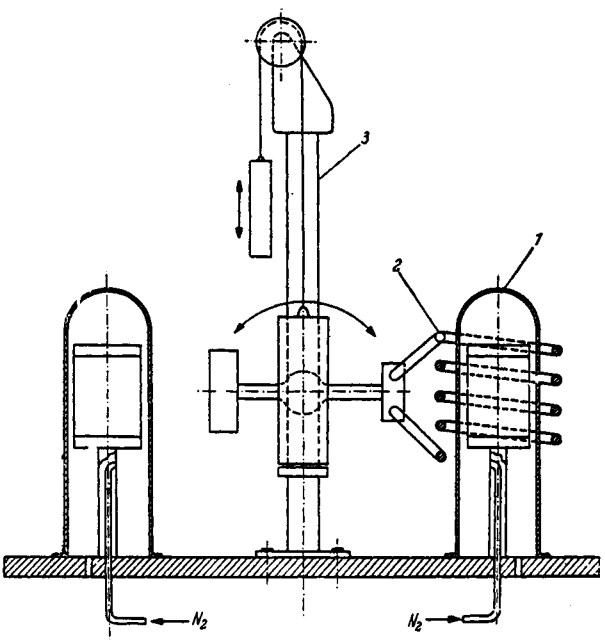


II

Fig. B 10-270 Serial production of sinter glass presses (KÜCHLI) (courtesy of BROWN BOVERI)

I manufacturing facility: on the right, six molds in position for heating, on the left, six others in cooling position, frame (with H.F. coils) can pivot; time for each row about 20 min. II arrangement seen from the side: *1* protective gas bell-jar with loaded mold of type shown in Fig. B 10-267; *2* H.F. work coil, which can be raised and then rotated over the rear line of bell-jars; *3* lift-and-tilt device, counterbalanced

[10.6]

(g) The dielectric constant ε is less than that of bulk glass of the same composition (Fig. B 10-270H).

(h) Loss factor $\tan\delta$ falls with rise in porosity, especially at low frequencies (Fig. B 10-270J). Comparison of $\tan\delta$ curves for K 707 and WoKa glass between 10^6 and 10^8 c/s shows that it is possible to replace a low-loss glass that is relatively hard to make (K 707) by a sinter glass made from ordinary hard glass (WoKa), since the

[10.6]

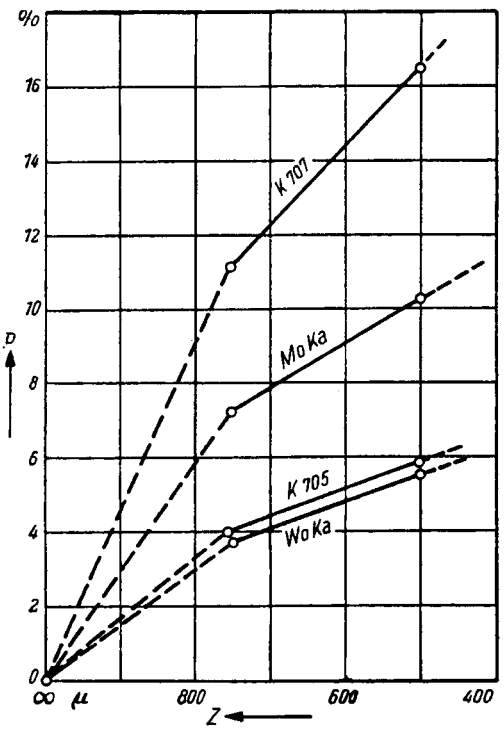


Fig. B 10-270A Porosity p[1] of vacuum-tight sinter glass of various types made in Czechoslovakia[2], p plotted as a function of maximum grain size Z of the starting grit. Sintering time 7–9 min. at 750–950° (1SLOSIAR)

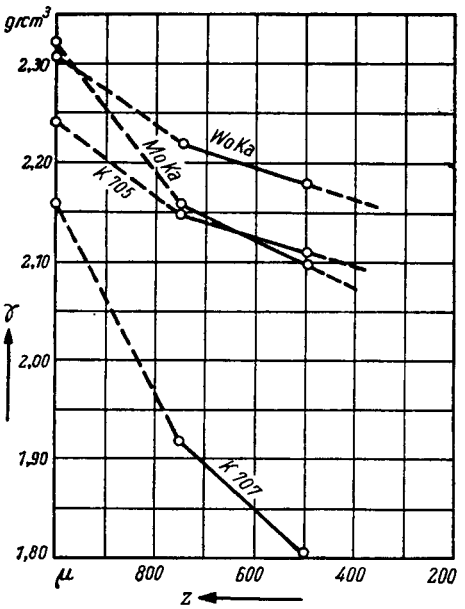
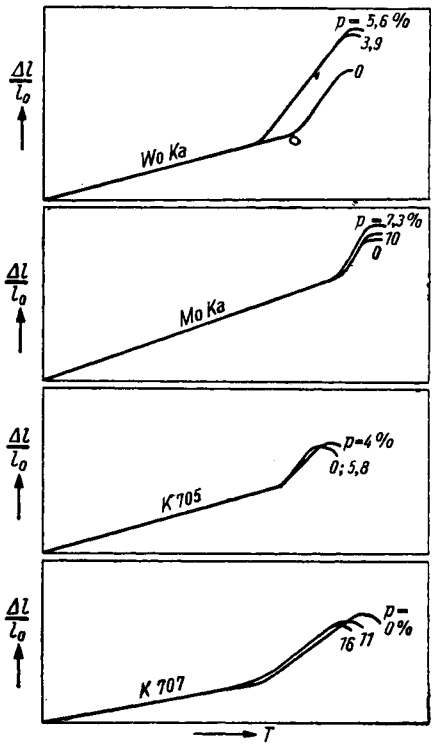


Fig. B 10-270B Density γ of vacuum-tight sinter glass as a function of maximum grain size Z of the starting grit (1SLOSIAR)
See notes to Fig. B 10-270A

(1) p = ratio of volume of sealed-off glass bubbles in the grit to the total volume of the grit.
(2) For composition see Table T 10-2, C.

latter (due to porosity) exhibits lower $\tan\delta$ values than bulk special glass of low loss factor; example: for bulk K 707 at 10^7 c/s, $\tan\delta$ is 16×10^{-4}, and for sintered WoKa (5.6% porosity) is 12×10^{-4}.

(i) The electrical rupture strength falls with rise in porosity (Fig. B 10-270K). According to 1DORGELO, a sinter glass with a *very large number* of evenly distributed bubbles (several thousand per mm³) should show the same value of E_d as solid, bubble-free



[10.6]

Fig. B 10-270C Thermal expansion characteristics of vacuum-tight sinter glass with various porosities p ([1]SLOSIAR)

See notes to Fig. B 10-270A. $p = 0\%$ for solid bubble-free glass

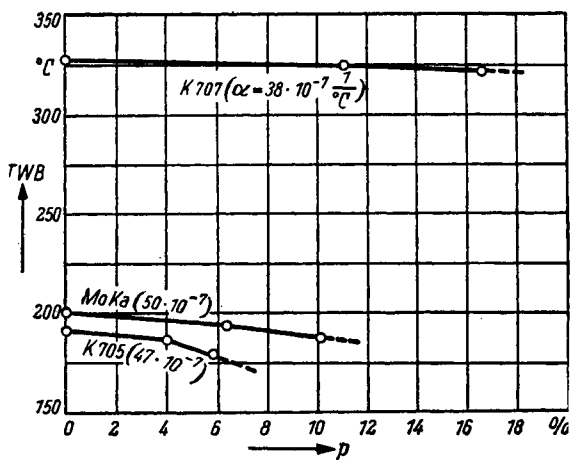


Fig. B 10-270D Thermal shock resistance (TWB)[1] of vacuum-tight sinter glass as a function of porosity p ([1]SLOSIAR)

[1] Measured in accordance with DIN 52 325. See notes to Fig. B 10-270A.

glass. This is because the potential difference between the glass surfaces in contact with the electrodes is distributed evenly over the many bubbles and is therefore so low for each bubble that there is no danger of ionization of gas in the bubble. In the case of sinter glass made from 200–750 μ grains, however, rupture strength always fell as porosity increased (see Fig. 10-270K and also Fig. B 10-79A).

[10.6]

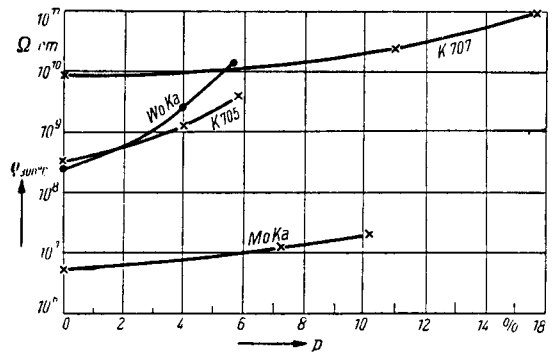


Fig. B 10-270E Electrical resistivity ϱ_{300} (at 300°) of some vacuum-tight sinter glasses as functions of porosity p (1SLOSIAR)

(k) In joints between sinter glass and metals or other glasses, which have αs different from the sintered product, it is surprising that mechanical stresses built up in sealing are much weaker in the corresponding solid (clear) glass; a search for the ex-

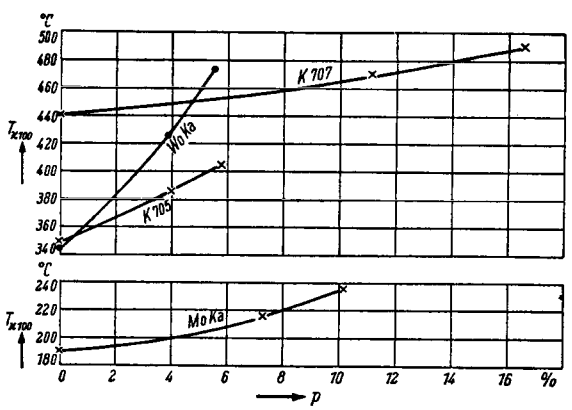


Fig. B 10-270F $T_{\varkappa 100}$ point for some vacuum-tight sinter glasses as functions of porosity p (1SLOSIAR)

planation will be found in 1DORGELO. Also, the sintered glass body can be cooled much faster after sintering or later sealing processes than can homogeneous components of clear glass, without dangerous stresses occurring.

The technique of making sintered glass presses is relatively reliable, particularly as a consequence of this latter effect; it does not require complex equipment nor skilled operatives, the shapes can be easily altered, and the dielectric and insulating properties

are good. These facts have led to wide application of sintered glass, especially in USW tube construction. Figure B 10-268 (I) shows a hard-glass sinter press-foot made by the H.F. process described; there are 5 Mo leads, a double coil ThW hot cathode mounted after the press was made; (II) shows a press of sintered Kovar glass powder with

[10.6]

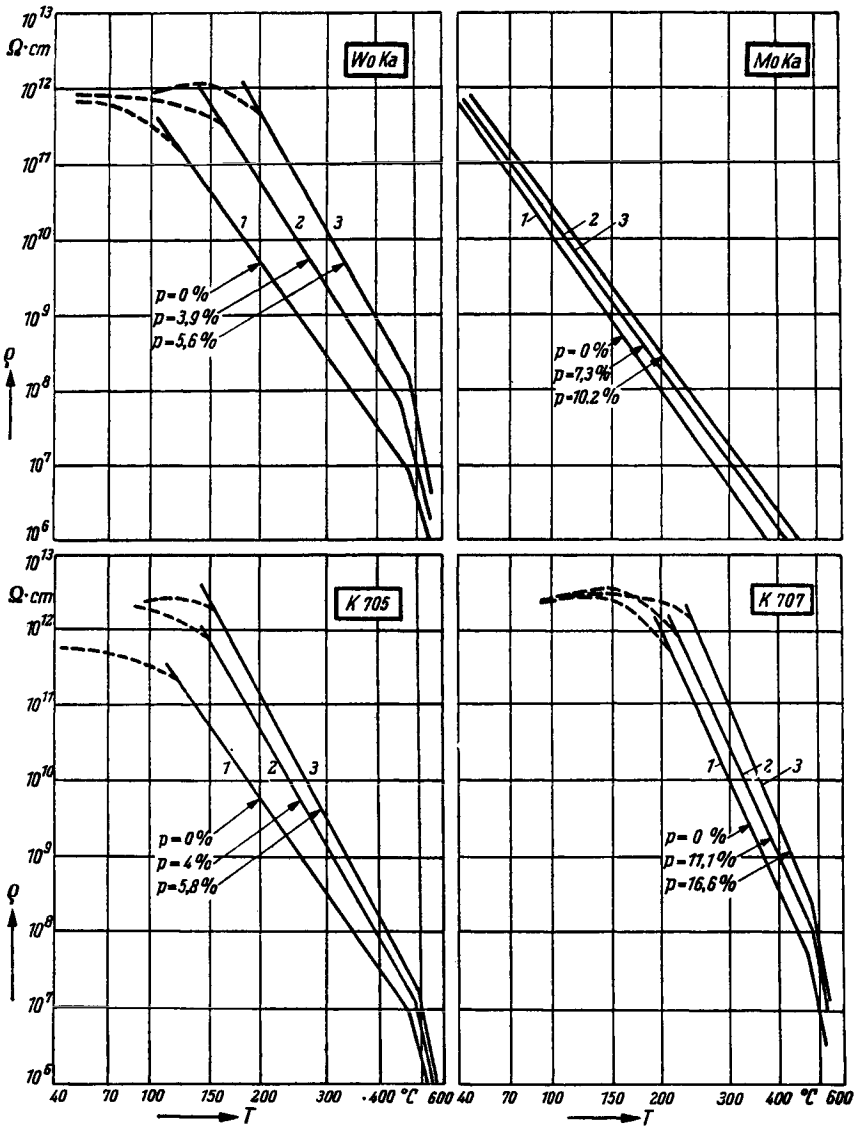


Fig. B 10-270 G Electrical resistivity ϱ of vacuum-tight sinter glasses of porosity p compared with clear glass of zero porosity and of the same type, as functions of temperature T ([1]SLOSIAR)

1 fused clear glass; *2* sinter glass from grit of maximum grain-size *ca.* 750 μ; *3* as *2*, *ca.* 500 μ

4 Kovar pins sintered into the press; Fig. B 8.5-24 shows a short-wave tube with sinter glass press.

Besides pins, lead-throughs of metal strip, tube, or plugs of suitable α can be sealed into the glass grit press; so also can ordinary, fused, solid glass (electrode supports). The number of leads and their arrangement are almost unlimited (see, e.g., Fig. B 10-271). Preformed exhaust stems can be sealed in as part of the grit sintering process, provided they are supported internally, by a coil of thin Ni wire for example (see Fig.

[10.6]

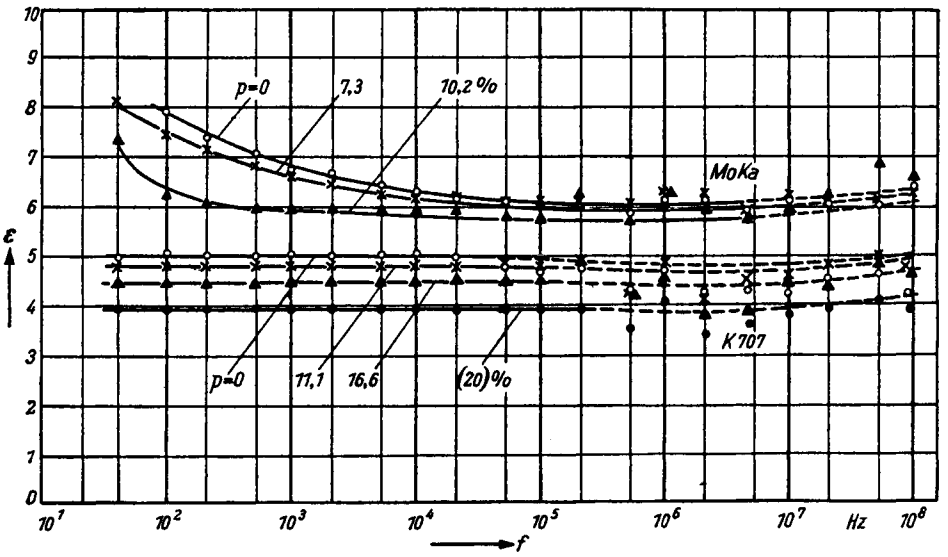


Fig. B 10-270 H Dielectric constant ε of two vacuum-tight sinter glasses with different porosity p, as functions of frequency f ([1] SLOSIAR)

B 10-272). Ni wire adheres only superficially and weakly to glass and can be withdrawn without much trouble after sintering. As an alternative, deformation of the stem can be prevented by closing its lower opening and filling with fine sand which is poured off after the sintering process. The exhaust stem can also be designed to support the tube or lamp mount (see Fig. B 10-272A). The figure shows a carbon-filament lamp, with three connecting pins in a low-capacitance sinter-glass press, a type with current-independent resistance over a wide range of power inputs, used at frequencies up to 30 mc/s as a H.F. resistance (2.75 Ω) for large transmitters, industrial generators and power measurements on artificial aerials. In addition to the conventional flat forms shown in Figs. B 10-268, B 10-271 and B 8.5-24, profiled sinter glass presses have proved successful, a cross-section of one example being shown in Fig. B 10-273. If such a press and its mount are sealed to a Kovar glass envelope so that the edge of the press surrounds that of the envelope, then the seal zone is put under compression because of the large shrinkage of sinter glass mentioned above; and apparently the resultant opposing tensile force on the central zone of the Kovar pin seals is reduced by annular relieving of the sintered foot, the so-called "annular groove" (in German: Ringgraben),

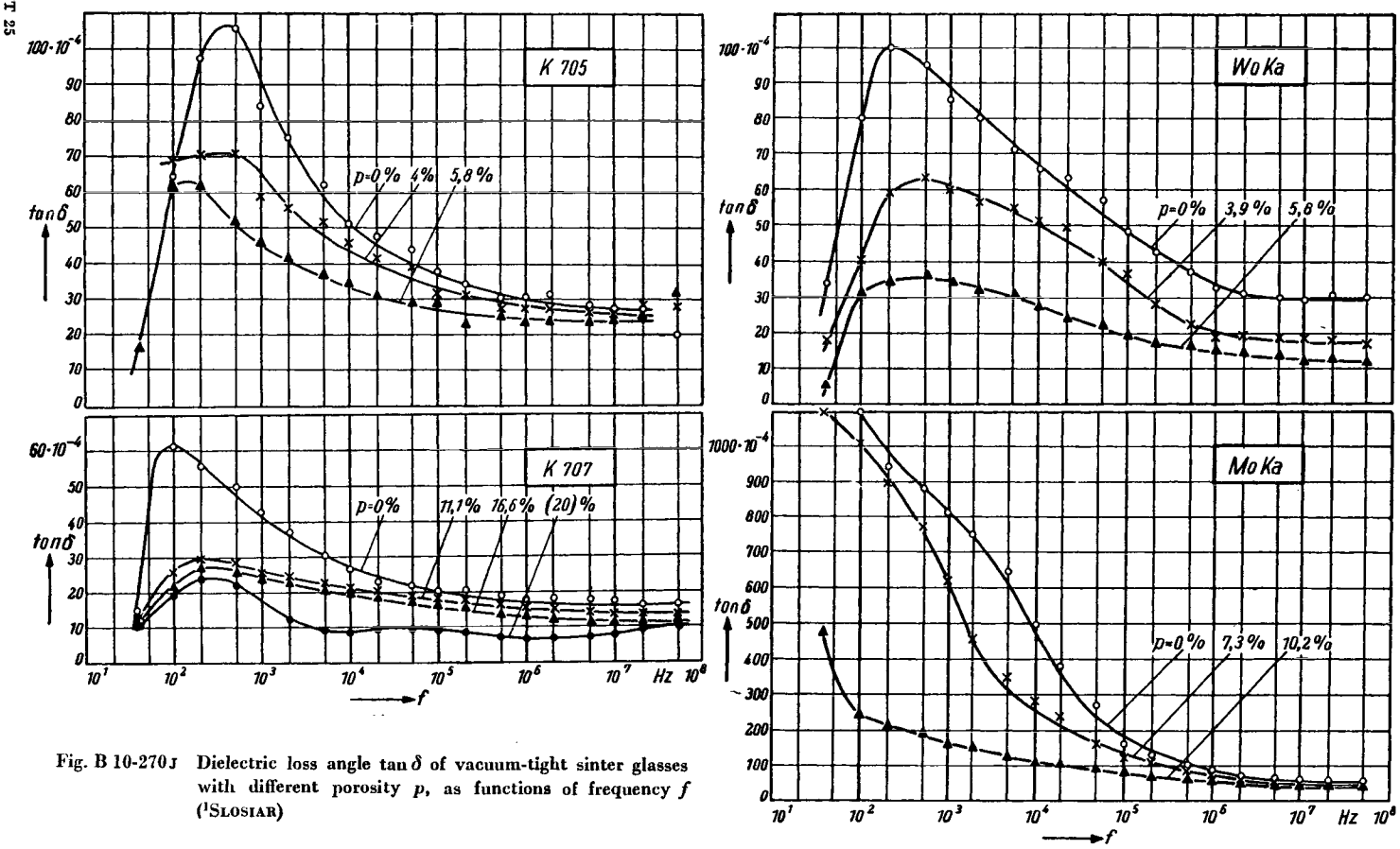


Fig. B 10-270 J Dielectric loss angle tan δ of vacuum-tight sinter glasses with different porosity p, as functions of frequency f (ISLOSIAR)

shown in Fig. B 10-273, *4*. Unfortunately, mechanical strains in opaque sintered glass cannot be detected by the ordinary polariscope. There are, however, developments under way in equipment using ultra-short waves for detection of such strains in opaque insulators, which clearly can be used for measuring strain in opal glass, sinter glass and ceramics (see, e.g., [3]DIETZEL).

Sinter glass technique permits constructions which would be very difficult to realize with standard presses made of fused clear glass, or would mean a relatively high reject rate. Figure B 10-274 gives an example. As in Fig. B 10-273, the process first involves
[10.6] fusing a clear-glass ring (2) to the sintered press (1); the other end of the ring is sealed

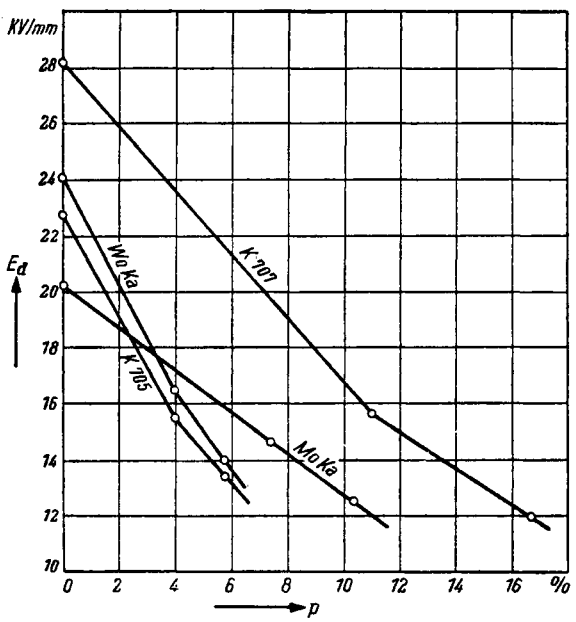
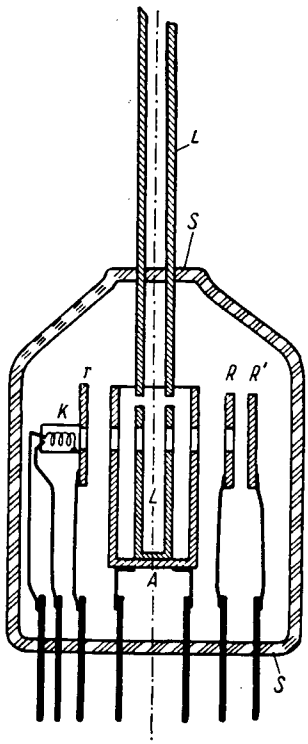


Fig. B 10-270K Electrical rupture strength E_d of vacuum-tight sinter glass as a function of porosity p ([2]SLOSIAR)
Test under oil on 2–3 mm thick glass disks at 50 c/s and 1 kV/sec voltage rise-time

vacuum-tight by the well-known Housekeeper technique to the edge (3) of a Kovar ring (4) (see Fig. B 5.4-15, F and Chapter 30 for this technique). When the electrode assembly has been mounted on the lead-throughs of the sintered press, a glass cap (5) sealed analogously to its own Kovar ring (6) is put over the electrode system, and the contacting surfaces of the rings (6) and (4) are brazed with a solder shim or ring (7) of AgCu eutectic, by pulsed H.F., to make a vacuum-tight joint (as shown in Figs. B 9.3-46 to B 10-47A). Defects in the electrode system can generally only be detected by final testing of the completed tube; if they occur, the USW tube, which may be very expensive, is not a total loss, but can often be unbrazed by pulsed H.F. under a protective gas, opened, and the electrode system trued up. The gas used in this case must be wholly free from cathode poisons; in particular, there should be no sulfur or impurities containing it, and this means no rubber lines should be used for gas inlet, since normal

rubber always contains sulfur. Obviously, it is also possible to reopen tubes whose filaments or cathodes have burnt out at the end of their operating life and which can therefore be repaired at only a fraction of the cost of making a new tube.



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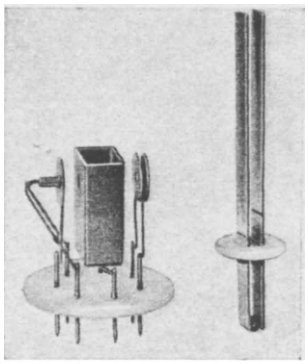

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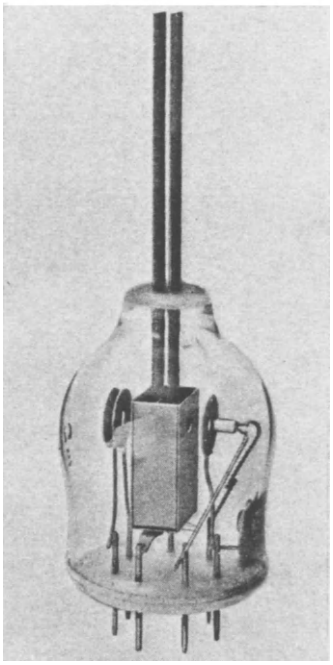


III

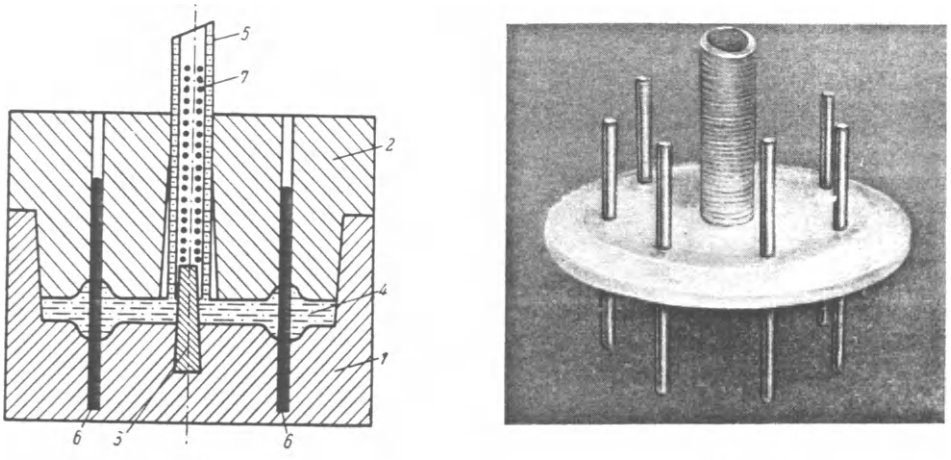
Fig. B 10-271 Oscillator tubes for very short waves (so-called "multireflex tubes") with two sinter glass lead-through disks (COETERIER)

I design: *K*, I.H. oxide cathode; *r* control electrode; *R*, *R'* reflecting electrodes; *A* plate; *L* Lecher wire system; *S* sinter glass. II upper and lower sinter glass disks with lead-throughs sintered in place. III view of completed tube (courtesy of PHILIPS)

[10.6]

It is possible to fuse the exhaust stem directly to the completed sinter glass press; the method is explained by Fig. B 10-275 in more detail: a graphite mold (*1*) is machined out to correspond with the work-piece and a steatite rod (*2*) is inserted centrally, while Kovar pins, pre-glassed with Kovar glass, are also placed in (*1*). The rod (*2*) is wound

[10.6]



I II

Fig. B 10-272 Sintering in an exhaust stem (clear glass) in manufacture of a press (sinter glass)

I manufacturing set-up (schematic) (STEYSKAL): *1* graphite mold, *2* cover; *3* stem mandrel of graphite *4* glass powder; *5* clear glass stem; *6* lead-through pins; *7* Ni wire support coil

II photograph of Kovar glass sintered press with six Kovar wire pins sintered in ([12]ESPE)

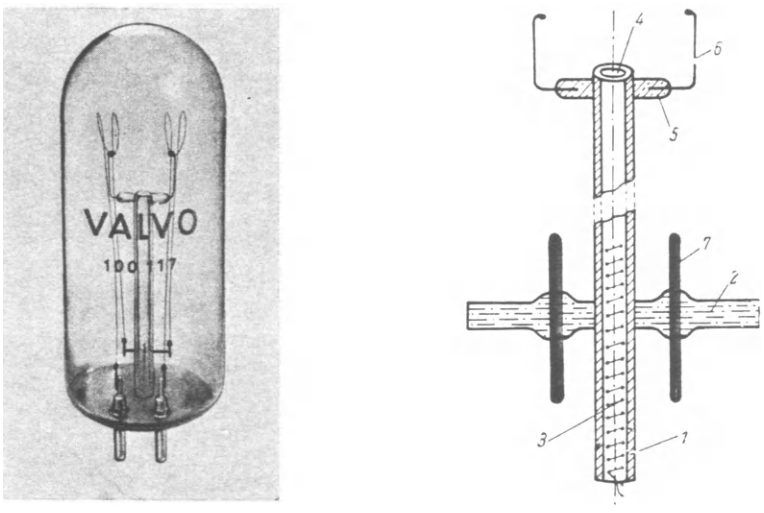
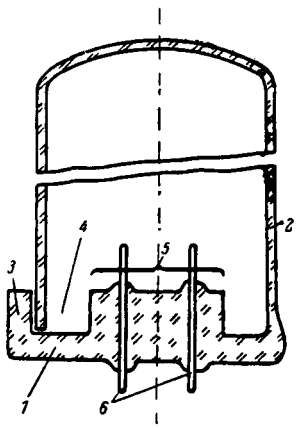


Fig. B 10-272A H.F. resistor (HV carbon-filament lamp) with low-capacitance disk foot of sinter glass (made by VALVO GmbH, Hamburg) (see also [17]ANON.)

The sintered-in exhaust stem is elongated and also serves to support the hooks for the two filaments that can be series or parallel connected

Right: design sketch: *1* exhaust stem centrally sintered to the foot *2*; *3* wire coil to support *1* during sintering; *4* orifice of *1*; *5* solid glass lugs (horns) with support hooks embedded; *6* hooks; *7* lead-throughs sintered to foot

with Fe wire (*3*) leaving no gaps between turns. Kovar glass grit (*4*) is poured into mold (*1*) and the press sintered to completion. After withdrawal of the cooled press, wire (*3*) is pulled off by a force applied along the axis of rod (*2*); there is no difficulty here be-



[10.6]

Fig. B 10-273 Sealing sinter glass press-foot (*1*) to envelope (*2*) of clear glass. Edge (*3*) of the press overlaps the edge of the envelope; an annular groove (*4*) is provided between (*3*) and the center of the press (*5*), in which pins (*6*) are sealed ([13]ESPE)

Left side of cross-section: before fusing; right side: after fusing. Pumping stem not shown in diagram

cause steatite ($\alpha = 80\times10^{-7}/°C$) and Fe ($\alpha = 130\times10^{-7}$) have much larger αs than Kovar glass ($\alpha = 48\times10^{-7}$) and therefore shrink more when the sinter glass is cooled. Generally, the ceramic rod then drops out of the press, and the edge of the glass flange (*5*) can be sealed by oxyhydrogen flame to an ordinary Kovar glass stem (*6*) slipped into

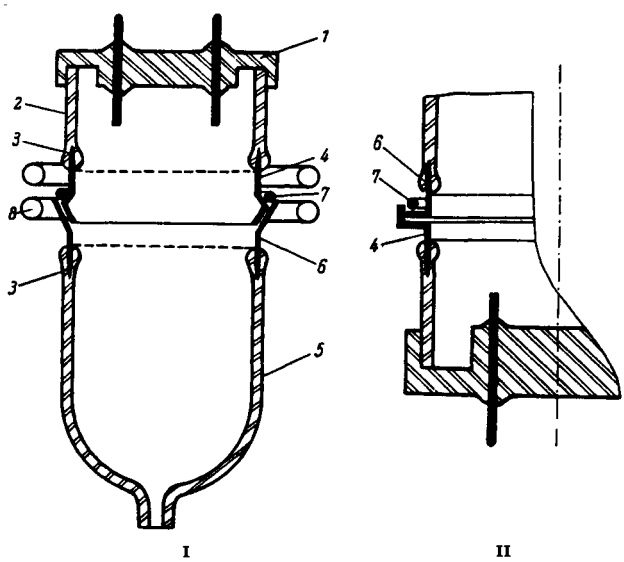


Fig. B 10-274 Short-wave tube with sintered press and envelope that can be soldered in place ([13]ESPE)

I *1* sintered Kovar glass press, sealed in as per Fig. B 10-273; *2* ordinary clear Kovar glass ring; *3* knife-edge seal; *4* Kovar ring; *5* ordinary Kovar glass envelope or cap; *6* Kovar ring sealed to envelope; *7* solder ring, AgCu eutectic (for brazing *7*, the tube base is placed on the top section as shown); *8* H.F. work coil for heating *7* by current pulse

II alternative form of braze area *7*, where lower Kovar ring *4* and upper Kovar ring *6* form a flange

the hole left by the rod (*2*). Figure B 10-276 shows a sinter glass foot with sealed-in clear glass stem and neck.

Another interesting example of the use of sinter glass is given in Fig. B 10-277. At one time, insulating bridges of solid glass rod (called "glass bead insulators") were

[10.6]

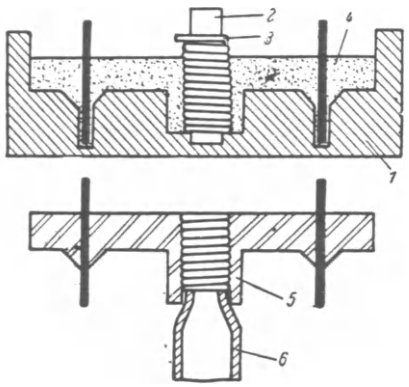


Fig. B 10-275 Making sintered press with exhaust stem ([13]ESPE)

1 sintering mold; *2* steatite rod, 4–5 mm dia.; *3* coil of Fe or Ni wire 0.2 mm dia.; *4* glass powder; *5* press flange with central hole after withdrawal of wire and rod *2* and sealing of ordinary Kovar glass stem

employed in making the electron gun of CROs; these are replaced here by sinter glass held in ceramic rods (Fig. B 10-277, IV). When sealing in the individual support wires, the ceramic rods filled with glass powder are heated till the glass is liquid and is retained in the groove by capillary forces. The glass flows round the ends of the wires, held in a jig at the correct spacings, and forms a strongly adherent bond with them after cooling.

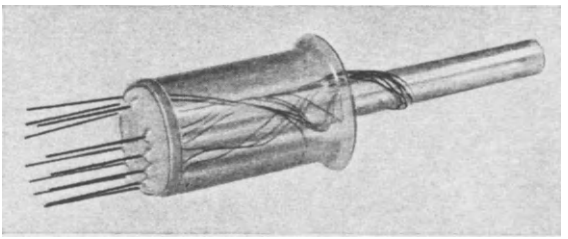


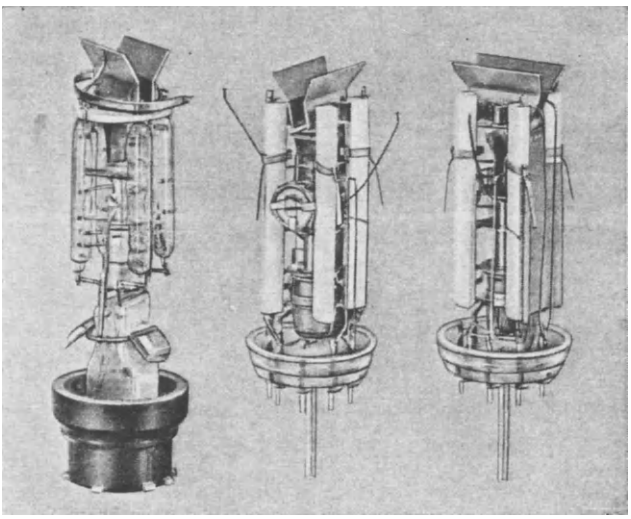
Fig. B 10-276 Profiled sinter glass press with 12 lead-through wires sintered in, with clear-glass neck and stem sealed to press ([1]DORGELO)

10.6.IV. *Multiform Glass* (*Ceramic Glass*)

The term should not be confused with the recent product "Pyroceram" ([3]CORNING, STOOKEY), a ceramic resulting from partial devitrification of glass, also called "glass ceramic" ([3]SHAND); cf. also 12.7. Ceramic glass means a material made from relatively fine-grain glass powder usually produced by ball-milling, and sized at less than 150 μ for the most part. The methods of manufacture are like those normally employed for ceramics for many years past, and are treated extensively in 12.1. The chief processes are called "slip-casting" from aqueous suspensions in plaster of Paris molds (12.1,III 2) and "dry molding" of mixtures of glass powder and organic binder. By these methods,

piece-parts are made which are then kiln-fired to high density somewhat above softening point, at the "sintering temperature" ($\eta = 10^6$ P, see Table T 10–5) of the glass concerned. These "ceramic" processes, especially slip-casting, are primarily suitable for

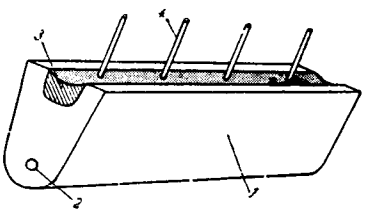
[10.6]



I II III

Fig. B 10-277 System for production and deflexion of electron beam in oscillograph tubes, the "electron gun" ([2]GIER)

I earlier construction with pinch and insulating bridges of glass (called "glass bead insulators"). II and III more recent constructions with dished foot, CrFe pins and electrode insulator supports of sinter glass held in ceramic rods as shown in IV. IV profile of insulator rods: *1* ceramic; *2* hole for support rod; *3* side groove filled with sinter glass in which support wires *4* are embedded



IV

TABLE T 10–37. COMPARISON OF PROPERTIES OF MULTIFORM CORNING GLASS 7761, MADE FROM FINE GLASS POWDER, WITH THOSE OF HOMOGENEOUS CLEAR GLASS 7761 (MCKNIGHT)

			SINTER GLASS MULTIFORM 7761	HOMOGENEOUS GLASS CORNING 7761 [1]
Density		g/cm³	2.12	2.23
Max. working temp.		°C	450	450
Softening temp.		°C	—	780
Expansion coeff. (0–300 °C)		1/°C	33×10^{-7}	33×10^{-7}
Elec. resistivity	230 °C	Ω-cm	10^{12}	$10^{9.4}$
	350 °C		10^{10}	$10^{7.7}$
Dielectric constant (10^6 c/s)		ε	4.0	4.5
Dielectric loss angle (10^6 c/s)		$\tan\delta$	10×10^{-4}	18×10^{-4}

[1] Very similar to CORNING borosilicate glass 7760, Table T 10–4, A 1.

high-silica, relatively water-resistant glasses ($SiO_2 > 96$ w/o). Multiform glasses have properties that differ only slightly from pure quartz glass (see Chapter 11).

Figure B 10-278 shows some piece-parts made from CORNING 7900 M multiform glass by molding and firing at 1200 to 1300°, with porosity about 1%. As can be seen, these

[10.6]

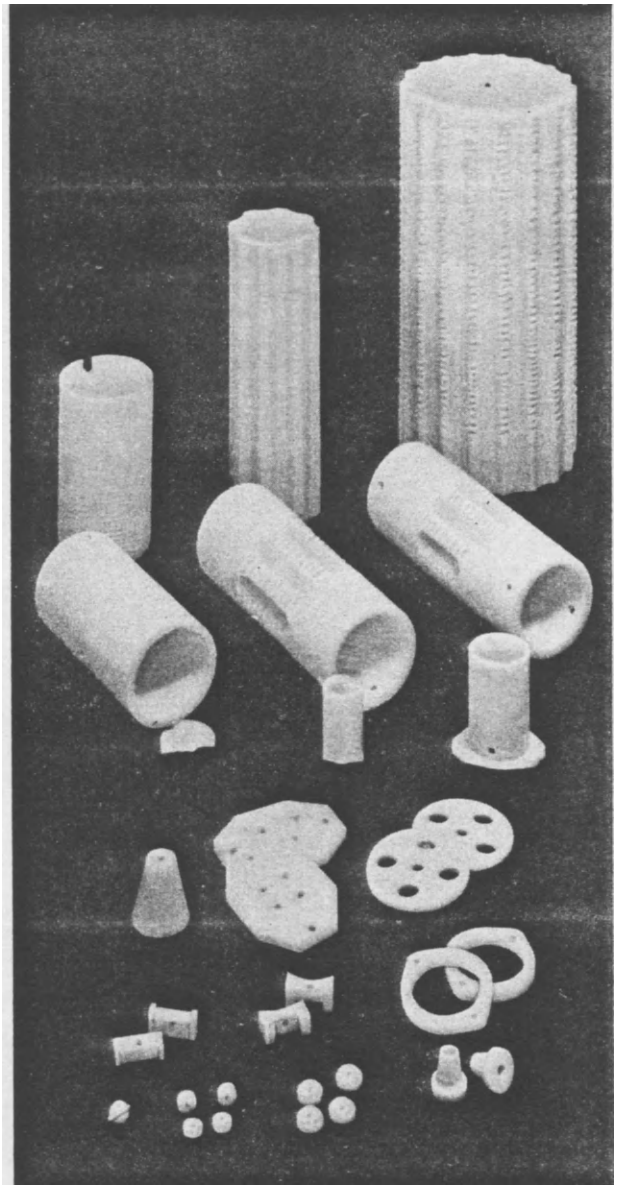


Fig. B 10-278 Multiform glass piece-parts made by dry molding and sintering (courtesy of CORNING GLASS WORKS)

bodies are not transparent, because of their internal air-bubbles, but are white, milky and translucent. Table T 10–4, 1, gives the properties of this glass (96% SiO_2). Recent precise measurements show that the α is only slightly higher than clear glass of the same composition, i.e. 8.5 instead of 7.8 (10^{-7}/°C). The same is true of electrical resistivity and dielectric loss. At room temperature the dielectric (rupture) strength is markedly lower, but at elevated temperatures, in the range of the so-called thermal breakdown in an electric field, is only a little less (see Fig. B 10-79A, cf. two dotted curves for 7790 clear and multiform). Mechanical strength properties of multiform glass are somewhat less than those of clear glass of the same composition, and depend strongly on firing [10.7] temperature.

Table T 10–37 compares properties of multiform made from CORNING 7761 with those of homogeneous fused clear glass 7761. The data essentially endorse the statements made in the previous section 10.6.III (sinter glass).

10.7 References

ACHESON, E. G. LTD.: *Techn. Bull.* **191**, p. 1, London, 1934 (Graphite coating of glass).

ADAM, H. *et al.: Glas- u. Hochvakuumtechnik* **1** (1952) 123–134 (Pressed glass to metal seals).

ADAMS, L. H., and E. D. WILLIAMSON: *J. Franklin Inst.* **190** (1920) 597, 835 (Principles of calculation of annealing schedules for glasses).

ALMA, G., and F. PRAKKE: *Philips Techn. Rdsch.* **8** (1946) 289–296 (Joining flat presses to envelopes with solder glass).

ALPERT, D.: *J. Appl. Phys.* **24** (1953) 874 (Helium permeability of glass at 20 °C).

ALPHEN, P. M. VAN: *Philips Techn. Rdsch.* **19** (1957/58), no. 2, p. 57 (Manufacture of bichromatic mirrors on glass by evaporation of thin layers in high vacuum).

ANDREWS, A. J.: *Enamels*, Illinois, 1937.

ANGERER, E. VON: edited by H. EBERT: *Technische Kunstgriffe bei physikalischen Untersuchungen*, 9th ed. (Braunschweig, 1954).

ANNEI, A. A.: *Uspechy chimii* **21** (1952) 469 (Current views on the nature of glass).

[1]ANON.: *Katalog technického skla československého sklařského průmyslu* (Prague, 1952).

[2]ANON.: *Engng.* **158** (1944) 495 (Properties of CHANCE sealing glasses for metal).

[3]ANON.: *Helios (Leipzig)* **14** (1935) 1373 (Universal glass-working machine).

[4]ANON.: *Die Technik* **8** (1953) 675 (Glass as a raw material).

[5]ANON.: *Light Metals* (Feb. 1943) 57–79 (Cathodic sputtering and vacuum evaporation of metals).

[6]ANON.: *Amer. Ceram. Soc. Bull.* **27** (1948) 353–362 (Dictionary of English technical terms relating to glass, with definitions).

[7]ANON.: *J. Soc. Glass Techn.* **35** (1951) 11; see also *Metal Progress* **63** (June 1953) 206 (Transparent, conducting glass, electrically heated).

[8]ANON.: *Glass* (Feb. 1950) 43–47 (Burners for glass-working).

[9]ANON.: *Philips Techn. Rdsch.* **14** (1953) no. 8, p. 235 (Bulb-blowing machine).

[10]ANON.: *Philips Techn. Rdsch.* **9** (1947) no. 7, p. 216 (Sealing electrodes into fluorescent lamps).

[11]ANON.: *Elect. Eng.* **24** (1952) 327 (Ribbon bulb-blowing machine).

[12]ANON.: *Philips Techn. Rdsch.* **8** (1946) 279 (Groups of machines for automatic manufacture of ordinary filament lamps).

[13]ANON.: *Philips Techn. Rdsch.* **13** (1952) 322 (Degassing furnace for X-ray tubes).

[14]ANON.: *Philips Techn. Rdsch.* **14** (1952/53) 81 (Automatic sealing machine for TV tubes).

[15]ANON.: *The Making of Reflecting Surfaces*; a discussion held by the Phys. Soc. (London) and the Opt. Soc. (London) 1920; cf. also GARDNER, I. C. and F. A. CASE: *The Making of Mirrors by the Deposition of Metals on Glass*, Circ. Bur. of Standards. no. 389 (Washington, 1931).

[16]ANON.: *Mat. and Methods* **43** (May 1956) 254 (Transparent, electrically-conducting thin Au layers deposited on glass by sputtering).

[17]ANON.: *Feinwerktechnik* **61** (1957) 65–66 (H.F. carbon-filament resistor, with sinter glass foot).

[18]ANON.: *Nickelberichte* **15** (1957) 251–254 (Ultrasonic drilling of glass and ceramics).

[19]ANON.: *Machinery* **90** (1957) 1196–1210 (Automatic production of TV receiver tubes by FERRANTI LTD, England).

[20]ANON.: *Engng.* **173** (1952) 701–703 (Vertical glass tube drawing machine).

[21]ANON.: *J. Soc. Glass Techn.* **40** (1956) 83P–104P (Measurement of glass viscosity; report by the Committee of the Soc. of Glass Techn., England).

ANTON, N.: *Ceramic Age* **63** (June 1954) 15–16, 18–19 (Solder glass paste for sealing mica windows to ceramic Geiger counters). [10.7]

ARDENNE, M. VON: *Tabellen der Elektronenphysik, Ionenphysik und Übermikroskopie* (Berlin, 1956) 645 (Evaporation furnace for mass-spectrometers).

ARMISTEAD, W. H.: US Pat. 2 414 504/1947 (Al_2O_3 glass with $\tan\delta < 6\times10^{-4}$).

[1]ASTM Designation C 158–43 (1943): *Standard Method of Flexure Testing of Glass, Determination of Modulus of Rupture.*

[2]ASTM Designation C 149–43: *Standard Method of Thermal Shock Test an Glass Containers.*

AWENDER, H. *et al.*: *Telefunken-Zeitg.* 28 H. 107 (1955) 34–38 (Evaporation unit for quartz oscillator crystals, with simultaneous tuning of the crystal).

BABCOCK, C. L., and I. V. HOFFACKER: *Phys. Rev.* **44** (1933) 321a; see also BABCOCK, C. L.: *J. Amer. Ceram. Soc.* **17** (1934) 329–342 (Measurement of the electrical conductivity of fused glasses).

BALLARD, W. E.: *Metal Spraying and Sprayed Metal*, 3rd ed. (London, 1948).

BALMFORTH, W., and I. A. HOLLAND: *J. Soc. Glass Techn.* **29** (1945) 111–123 (Photoelastic constants of glasses as functions of composition).

BANKROFT, G. H.: *Mod. Plastics* **31** (1935) no. 4, pp. 122–123, 210 (Metalizing plastic strip by HV evaporation).

BARR, W. E., and V. I. ANHORN: *Scientific and Industrial Glass Blowing and Laboratory Techniques* (Pittsburgh, 1949).

BARRER, R. M.: *Diffusion in and through Solids* (Cambridge, 1941).

BÁRTA, R.: *Sklářství a keramika* (*Glass and Ceramic*) Part IV (Prague, 1952).

BARTELS, H.: *Feinmechanik u. Präzision* **47** (1939) 219 (Measurement of strains in glass).

BAYFORD, L. I.: *Proc. Inst. Elec. Engrs.* III **99** (1952) no. 19, pp. 514–523 (Manufacture of TV tubes, cleaning in demineralized water).

BEATTIE, I. R.: *J. Soc. Glass Techn.* **37** (1953) 240–248 (Methods of determining hydrolytic resistance).

BECKER, A., and H. SALMANG: *Glastechn. Ber.* **7** (1929) 241 (Gas content of glasses).

[1]BELSER, R. B.: *Rev. Sci. Instr.* **25** (1954) 180–183 (Soldering thin metal layers to glass with indium and its alloys).

[2]BELSER, R. B., and W. H. HICKLIN: *Rev. Sci. Instr.* **27** (1956) 293–296 (Cathodic sputtering intensity of metals—comparative measurements).

BENNET, A. I.: *Vacuum* **3** (1953) 43–46 (Graphical methods for design of degassing furnaces).

BENSON, N. C. *et al.*: *J. Opt. Soc. Amer.* **40** (1950) 687–690 (HV evaporation of metals on to glass).

[1]BERGER, E., *et al.*: *Glastechn. Ber.* **12** (1934) 172 (Determination of transition temperature of glass by expansion and resistance measurements).

[2]BERGER, E.: US Pat. 1 961 603/1930/1934 (IR- absorbing phosphate glasses).

BERINSON, H.: *Szklo i Ceramika* (in Polish), no. 3 (1954) 48.

BESBORODOV, M. A.: *Strojenie stekla* (Moscow, 1953) (Structure of glass).

BEYERSDORFER, H.: *Silikat-Technik* **5** (1954) 459–462 (Electr. cond. of Jena optical glass).

BIOS Miscellaneous Report no. 101: *German Manufacture of Scales on Metal Glass and Celluloid* (London, 1946).

BLACK, H. R.: US Pat. 2 564 950/1947/1951 (X-ray glasses containing cerium).

BLECHSCHMIDT, E.: *Dissertation Jena* (1926); *Ann. Phys.* **81** (1926) 999 (Cathodic sputtering).

BLEEKSMA, J., *et al.*: *Philips Techn. Rdsch.* **10** (1948) 1–13 (Geiger counters for X-ray diffraction with Lindemann glass windows).

BLEIWEISS, I. L.: *Amer. Mach.* **93** (1949) no. 18, 118 (Vacuum evaporation of metals on glass, etc.).

BLEUZE, M. J., and M. P. DUSSAUSSOY: *Le Vide* **7**, no. 39 (May 1952) 1182–1190 (Technique for joining glass components with optically polished and heated contact surfaces).

[1]BLODGETT, K. B.: *J. Amer. Ceram. Soc.* **34** (1951) 14–27 (Surface conductivity of lead silicate glasses after H_2 reduction).

[2]BLODGETT, K. B.: *Phys. Rev.* **55** (1939) 391 (Anti-reflexion layers on glass with low refractive index).

BOETTCHER, A.: *Glastechn. Ber.* **25** (1952) 347–353 (Gas on glass surfaces and its removal).

BOGORODITSKY, N., and M. MALISHEV: *Techn. Phys. USSR* **2** (1935) 324 (Dielectric loss in glass).

BÖHM, H.: *Siemens-Z.* **29** (1955) 324–333 (Geiger counters).

BOLLENRATH, F.: *Metallkunde* (1933), H. 7; (1934) H. 3 (Description of an optical differential dilatometer).

BORGNIS, F.: *Helv. Phys. Acta* **22** (1949) 149–154 (Measurement of ε and $\tan\delta$ of glasses at 10^9 c/s and temperatures up to 350°). [10.7]

BORŠČEVSKIJ, S. M.: *Standartizacija* (1955) no. 1, 78 (Compositions of Russian glasses).

BOSCH, R.: DRP 555 295/26/32 (Vacuum switches with glass springs).

BRACKNEY, H., and Z. I. ATTLEE: *Rev. Sci. Instr.* **14** (1943) 59–63 (X-ray transmission of Lindemann glass).

BRADLEY, D. E.: *Brit. J. Appl. Phys.* **5** (1954) 65 (Vacuum evaporation of carbon).

BRAUN, E.: *Z. Techn. Phys.* **7** (1926) 505, 640 (Quartz dilatometer).

[1]BRITISH THOMSON-HOUSTON CO. LTD., Rugby, England: *BHT Colourless Glasses*; catalogue Dec. 1953.

[2]BRITISH THOMSON-HOUSTON CO. LTD.: Brit. Pat. 646 846/1947/1950; 647 414/1947/1950 (Production of conducting glass surfaces by reduction).

BRONSON, H. L.: quoted by A. W. HULL: *Physics* **2** (1932) 409, 420 (Insulating properties of glass in electrometer tubes).

BURDETT: *Infra-red-principle Gas Burners and Combustion Equipment* (Chicago, 1948).

BURGER, E. E.: *Gen. Elec. Rev.* **37** (1934) 93 (Expansion measurements on glasses and metals used in glass-metal seals).

BURGER, H. C., and P. H. VON CITTERT: *Z. Phys.* **66** (1930) 211 (Evaporation of quartz on Ag mirrors to protect against atmospheric effects).

CALDWELL, W. C.: *J. Appl. Phys.* **12** (1941) 779 (Evaporation of metals on to glass).

[1]CARTWRIGHT, C. H.: *Rev. Sci. Instr.* **1** (1930) 758 (Cathodic sputtering apparatus).

[2]CARTWRIGHT, C. H.: *Rev. Sci. Instr.* **3** (1932) 298 (Manufacture of W-heated Al_2O_3 crucibles for vacuum evaporation of metals).

[3]CARTWRIGHT, C. H.: reported in S. DUSHMAN: *Scientific Foundations of Vacuum Technique* (New York, 1949) 521–523.

CHEVENARD, P.: *Rev. de Métallurgie* **19** (1922) 39; **23** (1926) 92; *J. Phys. Radium* **7** (1926) 240 (Description of a dilatometer with mechanical recording).

CLAUSER, H. R.: *Mat. and Methods* (Feb. 1950) 72–82 (Enamels for Fe).

COETERIER, F.: *Philips Techn. Rdsch.* **8** (1946) 265, Fig. 9 (Use of sinter glass: lead throughs in USW tubes).

COHEN, A., and R. F. DORAN: *Amer. Ceram. Soc. Bull.* **33**, no. 1 (1954) 1–3 (Pressure testing TV tubes with resistance tensimeter strips).

[1] CORNING GLASS WORKS: Bulletin B-83: *Properties of Selected Commercial Glasses* (Corning, N.Y. 1949).

[2]CORNING GLASS WORKS: Brit. Pat. 674 565/1950/1952 (Forming glass cones for TV tubes by a centrifugal process).

[3]CORNING GLASS WORKS: *Pyroceram*; publicity brochure (Corning N.Y. 1957).

COUNTRYMAN, M. A.: *J. Appl. Phys.* **8** (1937) 432–433 (Wetting of heater wires by molten metals in vacuum evaporation).

COUSEN, A.: *J. Soc. Glass Techn.* **20** (1936) 418 (Effects of SO_2 on glass surfaces).

COWARD, I. N., and W. E. S. TURNER: *J. Soc. Glass Techn.* **22** (1938) 309 (Effects of SO_2 on glass surfaces).

CROOK, H. L.: *J. Soc. Glass Techn.* **23** (1939) 81–107 (Viscosity measurements on glass in the liquid range by stirrer method).

CROOKES, W.: *Proc. Roy. Soc.* (A) **50** (1891) 88 (Cathodic sputtering).

CURTIS, H. L.: *Bull. Bur. Standards* **11** (1914–1915) 359 (Surface resistivity of technical glasses).

[1]DALE, A. E., and J. E. STANWORTH: *J. Soc. Glass Techn.* **29** (1945) 77–91 (Glasses for metal sealing).

[2]DALE, A. E., and J. E. STANWORTH: *J. Soc. Glass Techn.* **29** (1945) 414–427 (Viscosity of glass in the annealing range).

[3]DALE, A. E., and J. E. STANWORTH: *J. Soc. Glass Techn.* **32** (1948) 147–153 (Properties and applications of solder glasses based on lead borate).
[4]DALE, A. E., and J. E. STANWORTH: *J. Soc. Glass Techn.* **33** (1949) 167–175 (Composition of solder glasses).
DALTON, R. H.: *J. Amer. Ceram. Soc.* **39** (1956) 109–112 (Solder glasses).
[1]DANZIN, A.: *Ann. Radioelectr.* **3** (1948) 153–168 (Glass properties and compositions).
[2]DANZIN, A.: *Silicates Industriels* **18** (1953) 321–324, 371–378 (Lead glasses with low α).
[3]DANZIN, A., and E. DESPOIS: *Ann. Radioelectr.* **8** (1948) 281 (Optically polished glass surfaces for vacuum-tight joints).
DARTNELL, R. C., *et al.*: *J. Amer. Ceram. Soc.* **34** (1951) 357–360 (Adherence of glass to tooling metals in glass-working).
[10.7] DAUDT, W., and H. EWEST: *Z. Techn. Phys.* **6** (1925) 329 (Outgassing of glass surfaces).
DAUVALTER, A. H.: *Stěkel. prom.* (in Russian) (1939) no. 11, pp. 28–31 (Glass annealing).
DAVIES, J. W., *et al.*: *Inst. Mech. Eng. Proc.* **158** (1948) 352–363 (Glass-working machines, enamel-to-metal bonds).
DEGUSSA, Frankfurt am Main: Technische Mitteilung No. 10: *Edelmetall-Präparate für die Elektro-Industrie*, Frankfurt a. M. 1958 (Noble metal preparations for the electrical industry).
DENTON, E. P., and H. RAWSON: *J. Soc. Glass Techn.* **40** (1956) 252–259 (Solder glasses for hard glass).
DIELS, K., and R. JAECKEL: *Leybold Vakuum-Taschenbuch* (Berlin, 1958) (Handbook of vacuum).
[1]DIETZEL, A.: *Naturwiss.* **29** (1941) 531 (Stereochemistry of glass).
[2]DIETZEL, A.: *Glastechn. Ber.* **22** (1948) 41 (Structure and properties of glass).
DIETZEL, A., and E. DEEG: *Glastechn. Ber.* **31** (1945) 396–404 (Detection and measurement of anisotropy in opaque, poorly-conducting materials); see also *Silikat-Technik* **6** (Sept. 1955).
DIN Norm 12111 (formerly DIN DENOG 62): *Glas für Laboratoriumsgeräte; Prüfverfahren: Hydrolytische Widerstandsfähigkeit* (Hydrolytic resistance of glass, test for).
DIN Norm 12116: *Glas für Laboratoriumsgeräte; Prüfverfahren: Säurebeständigkeit* (Acid resistance, test for).
DIN Norm 12122: *Glas für Laboratoriumsgeräte; Prüfverfahren: Laugenbeständigkeit* (Resistance to alkalis, test for).
DIN Norm 52325 (Feb. 1954): *Bestimmung der Temperaturwechselbeständigkeit* (Thermal shock resistance tests).
DOLEŽAL, V.: *Informativní přehled Výzk. úst. sklářský, Hradec Králové* (1954) 3–19 (Technical glasses with high alumina content).
[1]DORGELO, E. G.: *Philips Techn. Rdsch.* **8** (1946) 2–7 (Manufacture and properties of sinter glass).
[2]DORGELO, E. G.: *Philips Techn. Rdsch.* **10** (1949) 273–281 (Sealing metal to glass-powder).
[3]DORGELO, E. G.: quoted by J. M. STEVELS: *Verres et Réfractaires* **4** (1950) 3–9 (Search for explanation of low stresses in sintered disk presses of electron tubes).
[1]DOUGLAS, R. W.: *J. Sci. Instr.* **22** (1945) 81 (Applications of glass in HV technique).
[2]DOUGLAS, R. W.: *J. Soc. Glass Techn.* **29** (1945) 92–110 (Strains in glass-metal seals).
DOUGLAS, R. W., and I. O. ISARD: *J. Soc. Glass Techn.* **33** (1949) 289–335 (Dealkalization of glass surfaces with SO_2).
DRALLE-KEPPELER: *Die Glasfabrikation*, 2nd ed. (Munich, 1926) (Glass manufacture).
DUFOUR, CH.: *Le Vide* No. 16–17 (July-Sept. 1948) 480–486 (Evaporation of optical coatings on to glass).
DUNCAN, G. S.: *A Bibliography of Glass* (London, 1954).
DUSHMAN, S.: *Scientific Foundations of Vacuum Technique* (New York, 1949).
DÜSING, W.: *Telefunken-Zeitung* **26** (1953) 111–120 (Measurement of life of glass-metal seals under thermal and electrical loads).
[1]EBERT, H.: *Anleitung zum Gasblasen*, 6th ed. (Leipzig, 1926).
[2]EBERT, H., and S. ERK: *Glas u. Apparat* **16** (1936) 157 (Aging schedule for thermometer glass).
EDENS, A. H.: *Philips Techn. Rdsch.* **19** (1958) 271–277 (Machine for welding the cone to the panel of TV tubes with a burner).
[1]EISLER, CH.: US Pat. 1 522 001/24/25 (Pinching tool).
[2]EISLER, ENG. CO.: Catalog No. 103–53 (Newark, N. J. 1953).
ENDE, W.: *Z. Techn. Phys.* **15** (1934) 313 (UV transparent phosphate glass).
ENDELL, K.: *Ber. dtsch. Glas. Ges.* **13** (1932) 97 (Strains in glass).

[1]ENGEL, F.: *Glastechn. Ber.* **31** (1958) 133–137 (Measurements of strain in glass-metal seals at elevated temperatures with hot-stage polarization microscope).

[2]ENGEL, F.: *Vakuumtechnik* **8** (1959) 44–47 (Glass electrolysis in HV tubes through bombardment of the glass wall by stray electrons).

[1]ENGLISH, S., and W. E. S. TURNER: *J. Soc. Glass Techn.* **2** (1918) 90–102 (Determination of the softening point of a horizontal glass rod clamped at one end).

[2]ENGLISH, S., and W. E. S. TURNER: *J. Amer. Ceram. Soc.* **10** (1927) 551 and **12** (1929) 760 (Calculation of α for a glass from expansion coefficients of its components).

ERÖSS, D.: *Slabopr. obzor* **20** (1959) 110–117 (Resistance welding of glass).

[1]ESPE, W.: *Kovar, ein nützlicher Werkstoff der Hochvakuum- und Gerätebautechnik* (Füssen/Bayern, 1956) (For reference to same book in Czech, publ. 1953, see German text). [10.7]

[2]ESPE, W.: *Feritické chromželezo pro zátavy do skla ve vakuové technice* (Prague, 1953); Ferritisches Chromeisen für vakuumdichte Glas-Metall-Verschmelzungen, *Vakuumtechnik* **4** (1955) 82–100.

[3]ESPE, W., and V. KRATOCHVÍL: *Slabopr. obzor* **13** (1952) 181–189 (Glass-metal sealing in the manufacture of electron tubes).

[4]ESPE, W., and J. BÖHME: *Feinmechanik u. Präzision* **45** (1937) 57–60, 73–76, 101–104, 115–118 (Glass a material of vacuum technique).

[5]ESPE, W., and H. KOSACK: *Feinmechanik u. Präzision* **46** (1938) 329–334; **47** (1939) 1–6, 29–34 (Mechanical equipment for glass-working).

[6]ESPE, W.: *Feinmechanik u. Präzision* **47** (1939) 225–230, 247–252, 257–264 (esp. 229ff.: expansion measurements on technical glasses).

[7]ESPE, W.: *Werkstoffe der Elektrotechnik in Tabellen u. Kurven* (Berlin, 1954) (also in Czech, Prague, 1950) (Materials of electrotechnology).

[8]ESPE, W., and V. POKORNÝ: *Slabopr. obzor* **14** (1953) 178–187 (Construction of transmitter tubes).

[9]ESPE, W.: *Slabopr. obzor* **14** (1953) 531–547, also *Vakuumtechnik* **4** (1955) 10–24, 34–40 (Graphite molds for making sinter glass presses).

[10]ESPE, W.: DRP 695 623/32/40; French Pat. 760 692/32/34; Austrian Pat. 144 177/32/35 (Graphite coatings on glass for high-resistance leaks for charges built up on insulating parts of electron tubes).

[11]ESPE, W.: *Elektrotechnik Praha* **5** (1950) 258–262; *Feinwerktechnik* **55** (1951) 303–306 (Solder glass in vacuum technique).

[12]ESPE, W.: *Strojnoelektrotechnický časopis* **7** (1956) 193–200 (Sinter glass technique).

[13]ESPE, W., and B. HRZEK: *Strojnoelektrotechnický časopis* **8** (1957) 165–173 (Experimental studies in sinter glass technique).

[14]ESPE, W.: *Slabopr. obzor* **16** (1955) 430–434 (Glasses for vacuum technology made by firms in Czechoslovakia and the German Democratic Republic).

[15]ESPE, W.: *Über Aufdampfung von dünnen Schichten im Hochvakuum*; in M. AUWAERTER: *Ergebnisse der Hochvakuumtechnik u. der Physik dünner Schichten* (Stuttgart, 1957).

[16]ESPE, W., and J. SLOSIAR: *Vakuumtechnik* **8** (1959) 209–214; **9** (1960) 7–13 (Manufacture and properties of vacuum-tight sinter glass).

ETZRODT, A.: *Glas- u. Hochvakuumtechnik* **1** (1952) 85–91 (Temperature dependence of the electrical resistance of glasses).

FANDERLIK, M., O. PŘIDAL, and F. TRENZ: *Sklářské praktikum* (Prague, 1951).

FEHSE, A., and K. SCHRÖTER: *Techn.-wiss. Abh. Osram-Konzern* **2** (1931) 207; *Glastechn. Ber.* **10** (1932) 193 (Machining glass with Widia cemented carbide).

FISCHER, A.: *Z. Naturforschung* **9a** (1954), June (6), 508–511 (Thin semi-conductor layers on glass).

FLORENCE, I. M. *et al.*: *J. Amer. Ceram. Soc.* **31** (1948) 328–331; *J. Res. Nat. Bur. Standards* **45** (1950) 121–128 (IR transparency of glasses).

FOOTE, P. D. *et al.*: *Pyrometric Practice;* Technologic Papers Bur. of Standards **13** (No. 170) (Washington, 1921).

FORTEY, I.: *J. Soc. Glass Techn.* **29** (1945) 124–127 (Projection strain tester).

FRANK, W., and L. KRATZ: *Feinwerktechnik* **56** (1952) no. 5, pp. 125–129 (Special Jena glasses).

FRENCH, E. A. H.: *Z. Instrumentkunde* **45** (1925) 461 (Copperplating glass surfaces by wet chemical method).

FRIEDMAN, H.: *Electronics* (April 1945); 132–137 (Geiger counter tubes with Lindemann glass windows); see also US Pat. 2386785.

FRITZ-SCHMIDT, M. *et al.*: *Z. techn. Phys.* **11** (1930) 289 (Transmission of IR, UV and visible light through glass).

FRUTH, H. F.: *Bell System Techn. Jour.* **11** (1932) 283 (Cathodic sputtering apparatus).

FRY, H.: BIOS Report No. 1183, London 1947 (Antireflexion layers on glass).

FRYŠ, J.: *Abeceda smaltování* (*The ABC of enameling*), (Prague, 1955).

FULCHER, G. S.: *J. Amer. Ceram. Soc.* **8** (1925) 339–355 (Temperature dependence of viscosity of glass).

FULDA, M.: *Sprechsaal* **60** (1927) 769, 789, 810, 831, 853 (Electrical resistivity and surface conductivity for glasses of different composition).

[1]GALLUP, J.: *J. Amer. Ceram. Soc.* **29** (1946) 227–281 (Electrolysis of soft glass feet of rectifier tubes).

[2]GALLUP, J., and A. G. F. DINGWALL: *Ceram. Bull.* **36** (1957) 47–51 (Solder glasses).

[10.7] GARDNER, I. J., and F. A. CASE: Circ. Bur. Standards No. 389 (Washington, 1931) (Recipes for wet-chemical silvering of glass).

GAUSE, H.: *Polarisationmikroskopie* (Berlin, 1954).

[1]GEHLHOFF, G.: *Lehrbuch der technischen Physik*, Band III: *Die Physik der Stoffe* (Leipzig, 1928).

[2]GEHLHOFF, G., and A. THOMAS: *J. Soc. Glass Techn.* **11** (1927) 347–362 (Impact strength of glass, esp. opal types).

[3]GEHLHOFF, G., and A. THOMAS: *Z. Techn. Phys.* **7** (1926) 105–120 (Measurement of mechanical properties of glasses).

[4]GEHLHOFF, G., and A. THOMAS: *Z. techn. Phys.* **7** (1926) 260–278 (Measurement of viscosity of technical glasses).

[5]GEHLHOFF, G., and M. THOMAS: *Z. Techn. Phys.* **6** (1925) 544–554 (Electrical resistance of glasses as a function of composition).

GEVERS, M.: *Philips Res. Rep.* **1** (1946) 197, 279, 298, 361, 447 (Loss angle of glasses at low temperatures).

GIBSON, C. S.: *Nature*, **140** (1937) Aug., p. 279 (Manufacture of Au deposits on glass to room temperature from solutions of $Au((C_2H_5)_2Br)_2$ in ethanol).

[1]GIER, J. DE *et al.*: *Philips Techn. Rdsch.* **15** (1953) 60–71 (Sealing glass for steel chromed both sides by diffusion process).

[2]GIER, J. DE and A. P. VAN ROOY: *Philips Techn. Rdsch.* **9** (1947) 181–185 (Ceramic plus sinter glass combination as insulating bridges for electrode supports, esp. in electron guns).

[3]GIER, J. DE and J. A. M. SMELT: US Pat. 2477329/1948/1949 (Glass containing Ce to reduce blackening from X-ray and electron bombardment).

GLASWERK MAINZ des Jenaer Glaswerkes SCHOTT UND GEN., El. Dept.: private communication (1954).

GMELINS, *Handbuch der anorganischen Chemie*, 8th ed., volume entitled *Edelgase* (Berlin, 1926).

GODLEY, P.: *Iron Age* (April 1948); *Steel* (12 Dec, 1949), 84–86, 115–116 (Technique of evaporation of metals in high vacuum).

GOMER, R.: *Rev. Sci. Instr.* **24** (1953) 993 (Production of thin conducting SnO_2 layers by evaporation).

GOTT, O.: *Glastechn. Ber.* **24** (1951) 36 (Glasses with special spectral properties).

GOULD, C. E., and W. M. HAMPTON: *J. Soc. Glass Techn.* **14** (1930) 188–204 (thermal shock resistance of beakers).

GREEN, R. L., and K. B. BLODGETT: *J. Amer. Ceram. Soc.* **31** (1948) 89–100; also *Glass Ind.* **29** (1948) 395, 410 (Superficially elec. conducting glass).

GREENLAND, K. M.: BIOS Report 1215 (London 1946) (Evaporation of Rh, Al and antireflexion layers on glass, etc.).

GROSS, M. J.: FIAT Final Report No. 560 (London 1945), p. 13 (Solder glass).

GRUBE, G., and H. SPEIDEL: *Z. Elektrochem.* **53** (1949) 339 (Manufacture of SiO).

GRUNDMANN, W.: *Flüssigkeitsthermometrie*, 2nd ed. (Weimar, 1941).

GÜNTHERSCHULZE, A.: *Z. Phys.* **36** (1926) 563; **37** (1926) 868; **38** (1926) 575; **62** (1930) 607; **71** (1931) 279; **106** (1937) 371; **118** (1941) 145; **119** (1942) 95; *Vacuum* **3** (Oct. 1953) no. 4, p. 360–374 (Cathodic sputtering).

GUTHMANN, K.: *Stahl u. Eisen* **62** (1942) 477–482; **70** (1950) 116–118 (Temperature-indicating dyes and crayons).

GUTMAN, F., and L. W. O. MARTIN: *J. Sci. Instr.* **31** (1954) 221–222 (Electrolytic engraving on glass).

[1]GUYER, E. M.: *Trans. Electrochem. Soc.* **79** (1941) 187–198 (Electrical welding of glass by H.F.).

[2]GUYER, E. M.: *Electr. Eng.* **67** (1948) 446–447 (Resistance welding of glass by H.F. arc).

[3]GUYER, E. M.: *Electronics* (18 June 1945), 92–96; see also US Pat. 2306054/1942 (Resistance welding of hard glass after preheating by flame).

[4]GUYER, E. M. *et al.*: US Pat. 2389360/1945 (Resistance welding of glass by preheating with a graphite strip coating).

[5]GUYER, E. M.: *Proc. IRE* **32** (1944) 743–750 (Electrical properties, esp. surface conductance, of technical glasses).

HAAS, H.: *Polarisationsoptik* (Berlin, 1953).

HAASE, M.: *Glastechn. Ber.* **15** (1937) 295 (Polarizing filters and their applications).

HAGY, H. E., and H. N. RITLAND: *J. Amer. Ceram. Soc.* **40** (1957) 58–62 (Glass for sealing to FeCr alloy "430 Ti").

HALLA, F. *et al.*: *Monatsh. für Chemie* **81** (1950) 1092–1097 (Conductivity of molten glass). [10.7]

HAMAKER, H. C. *et al.*: *Philips Res. Rep.* **2** (1947) 171–176 (Poisoning of oxide cathodes by HCl vapor from glass envelopes containing NaCl).

HAMPTON, W. M.: *Illum. Engr. N. Y.* **26** (1933) 48 (Opal glass).

HÄNLEIN, W.: *Glastechn. Ber.* **28** (1955) 5–9 (Differential dialtometer with mechanical extensometer).

HARRIS, J. E., and E. E. SCHUMACHER: *Ind. Eng. Chem.* **15** (1923) 174 (Gas released from glass).

HARTMANN, H., and H. BRAND: *Glastechn. Ber.* (1953) 29–33 (Specific heat of technical glass).

[1]HASS, G.: *J. Amer. Ceram. Soc.* **33** (1950) 353–360 (Manufacture and applications of SiO).

[2]HASS, G., and H. KEHLER: *Optik* **5** (1949) 48 (SiO in electron microscopy).

HELDMAN, J. D.: *Techniques of Glass Manipulation in Scientific Research* (New York, 1946); 2nd ed. 1947.

HEPBURN, J. R. I.: *The Metallization of Plastics* (London, 1947).

HERITAGE, R. J., and I. R. BALMER: *Metallurgia* (Manchester) **47** (1953) 171–174 (Metalizing glass, ceramics and plastics).

[1]HERRMANN, H.: *Z. angew. Physik* **7** (1955) 174–176 (Measurement of strains in glass at elevated temperatures with the polarizations microscope).

[2]HERRMANN, H.: Techn. Informationsblatt **7** G 2 of VACUUMSCHMELZE, Hanau (Sept. 1955) (Color photographs of glass-metal seals by polarized light).

HETENYI, M.: *Handbook of Experimental Stress Analysis* (New York, 1950).

HEWLETT, C. W.: *Gen. Elec. Rev.* **50** (April 1947) 22–25 (Thallium sulfide photocells with support electrodes of Aquadag).

HIDNERT, P., and W. SOUDER: Dilatometry; in the *Metals Handbook* (1948 ed.) 168–174.

[1]HIESINGER, L. in: *Festschrift 100 Jahre Heraeus Hanau* (Frankfurt a. Main, 1951) 355–375 (HV evaporation technique).

[2]HIESINGER, L., and H. KÖNIG: *Festschrift 100 Jahre Heraeus Hanau* (Frankfurt a. Main, 1951) 376–392 (Cathode sputtering in reactive gases).

HILLIER, M., and R. L. BELL: *Brit. J. Appl. Phys.* **9** (1958) 94–97 (Composition of British Mo-sealing glasses).

HIPPEL, A. R.: *Dielectric Materials and Applications* (London, 1954).

HIX, A.: *Slabopr. obzor* **17** (1956) 690–697 (Sinter glass technique).

HOLLAND, A. I.: *Glass Rev.* **18** (1942) 94–100, 113–118, 132–156 (Manufacture and use of compensators in measurement of glass strains).

[1]HOLLAND, L.: *Vacuum* **2** (1952) 384 (Evaporation of alloys in vacuum).

[2]HOLLAND, L.: *Vacuum* **1** (1951) 23 (Evaporation of metals in vacuum).

[3]HOLLAND, L.: *J. Sci. Instr.* Suppl. no. 1 (1951) 59–62 (Commercial evaporation plant for blooming glass lenses).

[4]HOLLAND, L., and G. SIDDALL: *Vacuum* **3** (Oct. 1953) no. 4, ff. 375–391 (Highly transparent, low-resistance Au deposits on bismuth oxide substrates).

[5]HOLLAND, L., and G. SIDDALL: *Vacuum* **3** (July 1953) no. 3 ff. 245–253 (Deposition of thin metal oxide films by cathodic sputtering in noble gas $+O_2$ atmosphere); see also [4]HOLLAND.

[6]HOLLAND, L.: *Vacuum Deposition of Thin Films* (London, 1956).

[7]HOLLAND, L.: *Brit. J. Appl. Phys.* **9** (1958) 410–415 (Cleaning glass surfaces by glow discharge).

[8]HOLLAND, L. *et al.*: *Nature* **182** (1958) 851–852; *J. Sci. Instr.* **36** (1959) 105–116 (Getter pump with continuous feed of Ti wire whose end is evaporated by electron bombardment).

HOLLAND-MERTEN, E. L.: private communication of 29 March 1955 (Recent developments by DEUTSCHE VACUUMAPPARATE, Sangerhausen, GDR).

HOLZBECHER, K.: *Paliva* (1950) no. 5/6, 186–191 (Radiation burners).
HONIGMANN, L.: *Glastechn. Ber.* **12** (1934) 372–380 (Strain measurements in glass-metal seals).
[1]HOOD, H. P.: US Pat. 2410286/1943 (Low-loss glasses).
[2]HOOD, H. P., and M. E. NORDBERG: US Pat. 2 106 744/1934/1938, cf. US Pat. 2 215 039/34/40; 2 221 709/38/40; 2 286 275/40/42 (Vycor glass with $> 95\%$ SiO_2).
HOOLEY, I. G.: US Pat. 2 398 530/1941/1946 (UV-Transparent "black" phosphate glass).
HOWARD, L. A., and C. M. BERNTSON: *Rev. Sci. Instr.* **23** (1952) 383 (Ag as evaporant metal, electroplated on Mo heaters).
HÜBLER, A.: *Glas Email-Keramo-Technik* **3** (1952) 155–158 (Polishing glass with HF acid).
HÜBSCHER, M., and W. ROTHE: *Silikattechnik* (Aug. 1954), Suppl.: worksheet no. 105.
[10.7] HÜHN, C. F.: *Telefunken-Zeitung* **28** (1955) 215–222 (Bulb-sealing machines and in-line systems for TV tube manufacture).
HULBURT, E. O.: *Rev. Sci. Instr.* **5** (1934) 85 (Cathode sputtering technique).
[1]HULL, A. W., and E. E. BURGER: *Physics* **5** (1934) 384–405 (Metal-sealing glasses).
[2]HULL, A. W. *et al.*: *J. Appl. Phys.* **12** (1941) 698–707 (Glasses for glass-metal seals).
[3]HULL, A. W., and E. E. BURGER: *Rev. Sci. Instr.* **7** (1936) 98–100 (Strain testing with quartz wedge and polarization filter).
[4]HULL, A. W., and L. NAVIAS: US Pat. 2 272 747 (Fe-sealing glass).
HUNT, G. L.: BIOS Report no. 65, p. 10 (Ag sealing to OSRAM glass 424d at PHILIPS, Hamburg).
HUNTER, M. J. *et al.*: *Ind. Eng. Chem.* **39** (1947) 1389–1395 (Silicone treatment of glass surfaces).
HURSH, R. K.: *J. Amer. Ceram. Soc.* **32** (1949) 75–80 (Coating the inner surface of ceramic tube envelopes with Pt and Pd).
IKEDA, Y.: *J. Jap. Ceram. Assoc.* **58** (1950) no. 652, pp. 340–346 (Fe-sealing glass).
JAMIESON, W. D.: *J. Sci. Instr.* **35** (1958) 73 (Soft-solderable electrodeposited Cu coatings on glass or ceramics).
JEBSEN-MARWEDEL, H.: *Glastechnischer Fabrikationsfehler* (Berlin, 1936).
JENKEL, E., and A. SCHWITTMANN: *Glastechn. Ber.* **16** (1938) 163–170 (Viscosity measurements on glasses by glass fiber elongation method).
JEVSTROPJEV, K. S., and N. A. TOROPOV: *Chimija kremnija i fizitscheskaja chimija silikatov* (Moscow, 1950).
JIOA Report no. 9, London 1946 (Manufacture of Rh and Al mirrors and anti-reflexion coats on glass).
JOHANNSON, O. K., and I. I. TOROK: *Proc. IRE* **34** (1946) 296 (Production of water-repellent layers on glass by treating with liquid dimethyl silicones).
JOHNSON, J. R. *et al.*: *J. Amer. Ceram. Soc.* **34** (1951) 165–172 (Glass structure investigations with radio-isotopes).
JONAS, B.: *Philips Techn. Rev.* **3** (1938) 119–124 (W-intermediate glass-quartz seals).
KALPERS, H.: *Glas-Email-Keramo-Technik* **1** (1950) 8–9 (Heat-resistant steels for glass-molding).
KALSING, H.: *Sprechsaal* **86** (1953) 212–216, 339–341, 363–365, 389–392 (Metal-sealing glasses).
KARASEV, V. V., and G. I. IZMAJLOVA: *Žurn. techn. fiz.* **24** (1954) 871–874 (Cleaning glass surfaces by glow discharge).
KELLY, J. C.: *J. Sci. Instr.* **36** (1959) 89–90 (Evaporation of continuously-fed Zr or Ta rods whose ends are heated by electron bombardment).
KELLY, R. L., and P. I. RICE: *Rev. Sci. Instr.* **25** (1954) 391–392 (Alumina tube furnace with W heater wire and Ta insert for evaporation of Al).
KEPPELER, G.: *Sprechsaal* **61** (1928) 300 (Effect of SO_2 on glass surfaces).
KERSTEN, H., and C. H. DWIGHT: *J. Phys. Chem.* **35** (1933) 627–629 (Discoloration of glass by soft X-rays).
KEYWELL, F.: *Phys. Rev.* **87** (1952) 160; **97** (1955) 1611–1619 (Quantitative data on cathodic sputtering of Ag and Cu in inert gases).
KING, R. M.: *J. Amer. Ceram. Soc.* **19** (1936) 246 (Glass ground-coating enamels for sheet steel).
KINGSTON, W. E.: *Metal Progress* **44** (1943) 1115 (Recording dilatometer).
[1]KIRBY, P. L.: *Brit. J. Appl. Phys.* **1** (1950) 193–202 (Electrical conductivity of glass).
[2]KIRBY, P. L.: *J. Soc. Glass Techn.* **37** (1953) 3–6 (Measurement of electrical conductivity of glass with D.C.).
KITAIGORODSKIJ, I. I.: *Technologija stekla* (Moscow, 1951); Czech transl. *Sklo a tavení* (Prague, 1952); German transl. *Technologie des Glases* (Munich, 1957).
KLEMM, A., and E. BERGER: *Glastechn. Ber.* **5** (1927/28) 405 (Thermal expansion measurements on glass).

[1]KNAPP, O.: *Silikattechnik* **5** (1954) 51–54 (Properties and classification of glasses for use in vacuum technology).
[2]KNAPP, O.: *Silikattechnik* **6** (1955) 99–104 (Composition of glasses used in vacuum work).
[3]KNAPP, O.: *Acta Techn. Scient. Hungaricae* **8** (1954) 67–78 (Devitrification measurements on glasses of vacuum technology).
[4]KNAPP, O.: *Silikattechnik* (1958) 153–155 (Solder glasses).
KNEPPER, E.: *Die Fabrikation u. Berechnung der modernen Metalldrahtglühlampen* (Leipzig, 1926).
[1]KNOLL, M.: *Mechanismus der Kathodenzerstäubung*, Dissertation for the Techn. Hochschule (Munich, 1923).
[2]KNOLL, M.: DRP 522 836/1927/1932 (Cathode sputtering in flowing gas).
[3]KNOLL, M.: DRP 599 565/1931/1934 (Cathode sputtering apparatus).
KOCÍK, J., and J. NEBŘENSKÝ: *Sklář a keramik* **6** (1956) 273–278 (Glass with surface conductance). [10.7]
KOHL, W. H.: *Materials Technology for Electron Tubes* (New York, 1951).
KOHLRAUSCH, F.: *Praktische Physik*, 19th ed. (Leipzig, 1953).
KOHLSCHÜTTER, V.: *Z. Elektrochem.* **15** (1909) 316; *Jahrb. Radioaktivität* **9** (1912) 335 (Cathodic sputtering).
KOPEC, U.: *Deutsche Elektrotechnik* **11** (1957) 271–272 (Spectral transmission of various UV glasses).
KOROLEV, B. I.: *Osnovy vakuumnoj techniki*, 3rd ed. (Moscow, 1957).
KOSACK, H.: *Z. Feinmechanik u. Präzision* **44** (1936) 45 (Equipment for manufacture of HV devices).
KOTTE, I. I.: *Philips Techn. Rdsch.* **16** (1954) No. 1, p. 13 (Projection lamp with dome blackened by graphite coating).
[1]KRATOCHVIL, V.: *Zátavy chromželezného drátu*, 2nd ed. (Prague, 1950) (Sealing glass to CrFe wire).
[2]KRATOCHVÍL, V.: *Výroba elektronek a zářivek* (Prague, 1954) (Manufacture of electron and fluorescent tubes).
KREMENEZKY, J.: DRP 212 860/1908/1909 (Bulb-sealing by machine).
KRÜGER, F.: *Z. Techn. Phys.* **10** (1929) 495 (High-value resistors, made by sputtering).
KÜCHLI, G.: *Brown Boveri Mitteilungen* (1951), Heft 11, p. 342 (Sintering glass powder by H.F. in graphite molds).
KUSUNOSE, Y.: *Proc. IRE* **15** (1927) 431 (Short-wave puncturing of glass walls).
[1]LANGMUIR, I.: US Pat. 1 273 629/1918 (Degassing of filament lamp bulbs).
[2]LANGMUIR, I.: *Trans. AIEE* **32** (1913) 1921; *J. Amer. Chem. Soc.* (1916) 2221 (Gas released from filament lamp bulbs during degassing).
LAPORTE, H.: *Glas- u. Hochvakuumtechnik* **1** (1952) 20 (Glass compositions).
LAUDER, I., and E. C. M. GRIGG: *Rev. Sci. Instr.* **19** (1948) 371–372 (Working glass by combined flame and electrical radiant heating).
LAUG, E. P.: *Ind. Eng. Chem. Anal.* **6** (1934) 111 (Cleaning glass).
LAW, B.: *Rev. Sci. Instr.* **20** (1949) 958 (Quartz-coating metalized glass plates in ethyl silicate vapor).
LEHFELDT, W.: *Vortrag, Tagung Stanzereitechnik* (Nürnberg, 1956) (Ultrasonic drill for brittle materials such as metallic carbides, glass, ceramic).
LE MAY, R. C.: *Amer. Gas J.* (April 1951), 23–26, 42; see also *Glass Ind.* (July 1951), 339–344, 372, 373 (Gas-heated radiant burner).
LEVINSTEIN, H.: *J. Appl. Phys.* **20** (1949) 306 (Structure of evaporated metal layers).
LEWIS, W. K., L. SQUIRES and G. BROUGHTON: *Industrial Chemistry of Colloidal and Amorphous Materials* (New York, 1942) (Calculation of viscosity from rate of elongation of a heated glass fiber).
LIDDELL, D. M.: *Handbook of Nonferrous Metallurgy* (New York, 1945).
LIEDENEG, *Techn. Hochschule Graz*, quoted in CIOS Report XXXI-2, p. 31 (London, 1945).
[1]LILLIE, H. R.: *J. Amer. Ceram. Soc.* **16** (1933) 619–631 (Viscosity measurements on glass by the fiber method in the annealing range).
[2]LILLIE, H. R.: *J. Amer. Ceram. Soc.* **37** (1954) 111–117 (New determinations of the viscosity of technical glasses at the annealing and strain points).
[3]LILLIE, H. R.: *J. Amer. Ceram. Soc.* **14** (1931) 502–511 (Viscosity measurement on glass at the softening temperature by the method due to LITTLETON).
[4]LILLIE, H. R., and H. N. RITLAND: *J. Amer. Ceram. Soc.* **37** (1954) no. 10, pp. 466–473 (Fine annealing of optical glass).
[5]LILLIE, H. R.: *J. Amer. Ceram. Soc.* **35** (1952) 149–155 (Flow point of glass).
LINDEMANN, C. F., and C. A. LINDEMANN: *Z. Röntgenkunde* **13** (1911) 141 (Glass transparent to soft X-rays).
1LITTLETON, J. T., and G. W. MOREY: *Electrical Properties of Glass* (London, 1933).

[2]LITTLETON, J. T.: *J. Amer. Ceram. Soc.* **10** (1927) 259–263 (Measurement of softening point of glass by elongation of a glass rod); see also *Trans. Soc. Glass Techn.* **24** (1940) 176.

[3]LITTLETON, J. T., and E. H. ROBERTS: *J. Opt. Soc. Amer.* **4** (1920) 224–229 (Determination of the annealing point of glass).

LJUBIMOV, M. L.: *Spai metalla so steklom* (Moscow, 1957).

LOEBE, W., and W. LEDIG: *Z. Techn. Phys.* **6** (1925) 325 (UV transmission of glasses).

LUDWIG, CH.: *Fertigungstechnik* **3** (1953) 383–387 (Machining glass with carbide tools).

LUPÍNEK, M.: *Slabopr. obzor* **14** (1953) 28–36 (Glass-metal sealing by H.F.).

LUX, H.: *Anorganisch-chemische Experimentierkunst* (Leipzig, 1954).

LYSENKO, E.: *Žurn. techn. fiz.* **8** (1938) 1637 (Glasses with low dielectric losses).

[10.7] [1]MANNERS, M.: *Elect. Eng.* **24** (1953) 512–516 (British glasses for vacuum tubes).

[2]MANNERS, M.: *Times Rev. of Industry* (Jan. 1949), 22 (British solder glasses).

MARTI, O. K., and E. B. STEINBERG: US Pat. 2 459 828/1945/1949 (Internal enameling of metal pumping stems).

MASSACHUSETTS INST. OF TECHNOLOGY, Insulator Res. Lab.: *Table of Dielectric Materials*, Technical Report No. 10 (June 1948).

MASSEY, H. S. W., and E. H. S. BURHOP: *Electronic and Ionic Impact Phenomena* (New York, 1952) (pp. 578–594; mechanism of cathode sputtering).

MATHESON, W. G. in *1954 Vacuum Symposium Trans.* (Boston, 1955) (pp. 104–108; pumping systems in the lamp and tube industry).

MCKINNEY MOCHEL, J.: Canad. Pat. 466 320/1947/1950 (Production of thin, conducting SnO_2 layers on glass by spraying process).

MCKNIGHT, W. H.: *Mat. and Methods* **20** (Oct. 1934) 94–96 (Press-parts made of powder glass, "multiform glass").

MELNICK, L. M. *et al.*: *J. Amer. Ceram. Soc.* **34** (1951) 82–86 (Neutron-absorbing cadmium borosilicate glass).

MESMER, G.: *Spannungsoptik* (Berlin, 1939).

[1]METHFESSEL, S.: *Glas- u. Hochvakuumtechnik* **1** (1952) 6–8, 20–22 (Cathodic sputtering of metals).

[2]METHFESSEL, S.: *Dünne Schichten, ihre Herstellung u. Messung* (Halle, 1953).

[3]METHFESSEL, S.: *Glas- u. Hochvakuumtechnik* **2** (1953) 167–175 (Evaporation of metals on to glass, etc., in high vacuum).

MEUNIER, P.: *Ann. Radioelectr.* **4** (1949) no. 15, pp. 54–67 (Measurement of the electrical properties of glasses made in France).

MILLER, I. M., and B. SALZBURG: *RCA Rev.* **4** (1939) 486–504 ($\tan\delta$ of Corning glasses at 60 c/s and at elevated temperatures).

MILLNER, T., F. SZALKAY, J. PORUBSZKY, L. VÁMBÉRY and M. DÉRI: *Vakuumtechnika I* (Budapest, 1953).

MINDT, W.: *Glas u. Apparat* **9** (1928) 11 (Chemical surface treatment of glass).

MÖBIUS, P.: *Die Neon-Leuchtröhren* (Leipzig, 1932).

[1]MONACK, A. I.: *Glass Ind.* **27** (1946) 389–470, 476 (esp. 408–409: properties of Corning glasses).

[2]MONACK, A. I.: *Glass Ind.* **28** (1947) 21–25, 40, 42–44 (Metalizing glass and ceramics).

MÖNCH, G. CH.: *Hochvakuumtechnik* (Pößneck, 1950).

MOON, P. H., and A. S. NORCROSS: *Elect. Eng.* **49** (1930) 755–762 (Breakdown strength of glasses).

MORAVEC, J.: *Pokovovanie odparením vo vakuu* (*Metalization by vacuum evaporation*) (Bratislava, 1956), published by S.U.T.E.In.

MOREY, G. W.: *The Properties of Glass*, 2nd ed. (New York, 1954).

MÜLLENSIEFEN, W., and K. ENDELL: *Glastechn. Ber.* **11** (1933) 161–170 (Viscosity measurements on technical glasses in the liquid range, with a rising-ball viscosimeter).

MURGATROYD, I. B.: *J. Soc. Glass Techn.* **14** (1930) 2–16 (Annealing commercial glassware).

MURPHY, J. R.: *Glass Ind.* **31** (1950) 250–253 (Coating surfaces of metal molds for glass with colloidal graphite layers).

MYLIUS, F., and A. MAZZUCCHELLI: *Silikat-Ztg.* **1** (1913) 2 (Hydrolytic classification of glass).

NATIONAL RESEARCH CORP.: *J. Sci. Instr.* **24** (1947) 278 (Protection of metalized glass surfaces with SiO evaporation).

NAVIAS, L., and R. L. GREEN: *J. Amer. Ceram. Soc.* **29** (1946) 267 (Dielectric properties of glass at UHF and their dependence on composition).

NEPPIRAS, E. A., and R. D. FOSKETT: *Philips Techn. Rdsch.* **19** (1957/58) 37–48, 98–110 (Ultrasonic machining).
NICOLL, F. H.: *RCA Rev.* **10** (1949) 440–447 (Anti-reflexion layers on glass by chemical means).
NOKES, M. C.: *Modern Glass Working and Laboratory Technique* (London, 1937).
NORDBERG, M. E.: *J. Amer. Ceram. Soc.* **30** (1947) 174–179 (UV glasses for Hg lamps).
[1]NORTON, F. J.: *Gen. Elec. Rev.* **47** (1944) 6–16, also US Pat. 2 386 259/1945 (Production of "dry film" on glass or ceramic, properties of materials so treated).
[2]NORTON, F. J.: *Gen. Elec. Rev.* **47** (1944) no. 8, p. 47 (Surface treatment of glass or ceramic with silicone "dry film").
[3]NORTON, F. J.: *J. Amer. Ceram. Soc.* **36** (1953) 90–96 (Diffusion of gases, esp. He, through technical glasses); see also *J. Appl. Phys.* **28** (1957) 34–39. [10.7]
[4]NORTON, F. J.: *J. Appl. Phys.* **28** (1957) 34–39 (Gas permeability of solid materials).
NOVOTNÝ, A.: *Základy technologie smaltování* (*Principles of Enameling Technology*) (Prague, 1951).
NÜRNBERGER, C. E., and R. LIVINGSTON: *J. Phys. Chem.* **41** (1939) 691–697 (X-ray discoloration of glass).
OCHOTIN, M. W.: *Steklo i keram. prom. Moscow* **4** (1947) no. 11, pp. 8–9; *idem* **7** (1950) no. 5, pp. 6–7 (Viscosity of glasses from nomograms; for abstract see *Silikattechnik* **5** (1954) 503–504).
OEHME, F., and H. P. FREY: *Chem. Techn.* **8** (1956) 498–499 (Ag-coating of glass by firing-on).
OLSEN, L. O. *et al.*: *J. Appl. Phys.* **16** (1945) 425 (Vacuum evaporation of metals).
[1]ONDRÁČEK, M.: *Slabopr. obzor* **16** (1955) no. 7, pp. 370–377 (Construction of two units for measurement of glass viscosity by stirrer and fiber-drawing methods).
[2]ONDRÁČEK, M., and F. KVARDA: *Sklář a keramik* **7** (1957) 359–362 (Measurement of electrical resistivity of technical glasses).
OSRAM-G.E.C. GLASSWORKS (England): Techn. Information Pamphlet 1230 (Wembley, 1950).
OSRAM-KOMMANDIT-GES. BERLIN, *Osram glasses*, Techn. Inf. 11370.2.39 (Berlin, 1939).
OSTRANDER, G. D.: *Radio-Electronic eng.* (Aug. 1953) pp. 8 and 25 (Testing implosion strength of TV tubes).
PADMOS, A. A., and I. DE VRIES: *Philips Techn. Rdsch.* **9** (1947/48) 277–258 (Strain-testing glass).
PARKER, H. W., and F. J. FOX: *Proc. IRE* **21** (1933) 710 (Spraying electron tubes with metal).
PARTRIDGE, J. H.: *Glass-to-Metal Seals* (Sheffield, 1949).
PASK, J. A.: *Product Engng.* (Jan. 1950) pp. 129–134 (Expansion characteristics of Corning glasses)
PATNODE, W. I.: US Pat. 2 306 222/1940/1942 (Water-repellent silicone layers on glass).
PEDDLE, C. J.: *J. Soc. Glass Techn.* **21** (1937) 177 (Effect of SO_2 on glass surfaces).
PETZOLD, A.: *Email* (Berlin, 1955) (Enamels).
PEYSSON, J.: *Ann. Radioelectr.* **3** (1948) 107–114 (Electrolytic phenomena in glasses).
PHILIPS: DRP 427 354/22/26, DRP 466 639/25/28 (Automatic pumping equipment).
PHILLIPS, C. J.: *Glass, The Miracle Maker*, 4th ed. (London, 1941).
PILLER, H.: *Grundlagen u. Methoden der Untersuchung mit dem Polarisationsmikroscop* (Published by the Zeiss Company).
PINKUS, A. G.: US Pat. 2 381 925/1941/1945 (HF-resistant phospbate glass).
PIPKIN, M.: *Gen. Elec. Rev.* (March 1949) pp. 14–17 (Internal coating of filament lamps with silica particles).
POOLE, J. P.: *J. Amer. Ceram. Soc.* **32** (1949) 215–220 (Viscosity measurements by the glass fiber method).
[1]PRESTON, F. W.: *J. Appl. Phys.* **13** (1942) 623–634 (Mechanical properties of glass).
[2]PRESTON, E.: *Proc. Phys. Soc. Lond.* **53** (1941) 568–584 (Viscosity of glasses with various Na_2O contents).
PRESTON, I. S., and E. J. GILLHAM: *Proc. Phys. Soc. Lond.* **65** B (1952) 649 (Transparent, conducting films on glass).
PTR (Phys.-Techn. Reichsanstalt Berlin): *Z. Instrkde.* **49** (1929) 174 (Sputtering).
RANC, M. G.: *Le Vide*, nos. 40–41 (July-Sept. 1952) 1211–1219 (Properties of evaporated metal layers).
RASCH, E., and W. HINRICHSEN: *Z. Elektrochem.* **14** (1908) 41 (Conductivity of glass as a function of temperature).
RAVIČ, M. B.: *Poverchnostnoe bezplamennoe goranie* (*Flameless-surface heating process*) (Moscow-Leningrad, 1949).
READ, W. T.: *J. Appl. Phys.* **21** (1950) 250–257 (Strain measurements of glass bulbs).
REDSTON, G. D., and J. E. STANWORTH: *J. Soc. Glass Techn.* **32** (1948) 32–39 (Simple annealing schedule for technical glasses).
REICH, G.: *Vakuumtechnik* **3** (1955) no. 8, pp. 147–152 (In-line pumping systems for large tubes, esp. TV tubes).

REICHELT, W.: *Z. Metallkde.* **46** (1955) 268–271 (Vacuum evaporation for industrial surface finishing).
REIMANN, A. L.: *Vacuum Technique* (London, 1952).
RETZOW, U.: *Die Eigenschaften elektrischer Isoliermaterialien in graphischen Darstellungen* (Berlin, 1927).
[1]RICHARDSON, H. K.: *Ceram. Ind.* **52** (1949) no. 3, pp. 89–90 (Burners for glass-working).
[2]RICHARDSON, H. K.: *Amer. Ceram. Soc. Bull.* **29** (1950) 20–26 (Radiant gas burners for glass annealing).
RICHTER, K.: *Koll.-Z.* **61** (1932) 217 (Sputtering with heated cathode of thin Ag wires).
RIECK, G. D., and L. H. VERBEEK: *Philips Techn. Rdsch.* **12** (1951) 189–197 (Photoflash lamps with shatter-proofing lacquer).
RIEDMÜLLER, R.: *Ann. der Phys.* **20** (1934) 377 (Masks for use during pre-outgassing stage of evaporation of metals on to glass).
[10.7] RINDONE, G. E. *et al.*: *J. Amer. Ceram. Soc.* **30** (1947) 314–319 (Glass electrolysis).
RINNE, F., and M. BEREK: *Anleitung zur optischen Untersuchung mit dem Polarisationsmikroscop* (Stuttgart, new ed. 1953).
ROBINSON, H. A., and C. A. PETERSON: *J. Amer. Ceram. Soc.* **27** (1944) 129–138 (Viscosity measurements with the glass fiber method).
ROEPER, E.: *Glas-Email-Keramo-Technik* **8** (1957) 390–391 (Glass-wall thickness-gauge).
ROGERS, A. F., and F. P. KERR: *Optical Mineralogy* (New York, 1942).
ROGERS, W. A. *et al.*: *J. Appl. Phys.* **25** (1954) 868–875 (He-permeability of Pyrex).
ROIG, R., and E. COLLET: *Compt. Rend. Acad. Sci.* **234** (1952) 1677 (Silver-plating W wires for metal evaporation heaters).
RÖSCH, R. G., and O. H. KNOLL: *Z. Instrkde* **58** (1938) 181 (Dichromatic flat polarizers, their properties and uses).
ROSE, K.: *Mat. and Methods* **28** (Dec. 1948) 85–87 (Making Al mirrors on glass).
ROSS, A.: *Vakuumtechnik* **8** (1959) 1–11 (Vacuum evaporation of thin layers of inorganic materials).
ROTHERMEL, J. J. *et al.*: *J. Amer. Ceram. Soc.* **32** (1949) 153–162 (X-ray absorber glass with additions of lead oxide and tungsten oxide).
[1]ROTTGARDT, K.: DRP 492 768/26/30 (Automatic pumping system).
[2]ROTTGARDT, K. H. J., W. BERTHOLD and H. LUTZ: *Fernsehbildröhren für Schwarz-Weiß-Fernsehen* (Berlin, 1956).
RUSS, A.: *Sprechsaal* **61** (1928) 908 (Thermal conductivity of glasses).
RUSSELL, R.: FIAT Report No. 617, esp. pp. 32–38 (Manufacture and composition of Ag, Au and Pt lusters for metalizing glass or ceramic).
SCHILL, F.: *Informativní přehled* (*Výzkumný ústav sklářský Hradec Králové*) **1** (1953) 6–28 (Annealing glass).
[1]SCHMIDT, R.: *Das praktische Glasschmelzen*, 4th ed. (Dresden, 1951).
[2]SCHMIDT, R.: *Glastechn. Ber.* **15** (1937) 89 (Na-resistant glass).
SCHOLES, S. R.: *Modern Glass Practice* (Chicago, 1935).
SCHÖNBORN, H.: *Glastechn. Ber.* **15** (1937) 57–70 (Thermal shock resistance of technical glasses).
SCHOTT U. GENOSSEN: *Physikalische Eigenschaften der Jenaer Einschmelz- u. Zwischengläser*, publicity pamphlet (Jena, 1941).
SCHULZ, H.: *Glas* (Munich, 1923).
SCHULZE, D.: *Chem. Techn.* **8** (1956) 341–346 (Manufacture, properties and applications of SiO).
SCHWARZ, R., and J. HALBERSTADT: *Z. anorg. allgem. Chemie* **210** (1933) 286 (Glass electrolysis).
SCHWARZ-BERGKAMPF, E.: DRP 750 168/1937/1944; DRP 751 194/1939/1944 (Pre-enameling of sealing zones of metals before joining to glass).
SEDDON, E. *et al.*: *J. Amer. Soc. Glass Techn.* **16** (1932) 450 (Electrical resistivity of sodium silicate glasses).
SEITER, J. G., in *1954 Vacuum Symposium Trans.* (Boston, 1955) (pp. 116–120: metal evaporation plant).
SEREN, L.: *Rev. Sci. Instr.* **19** (1948) 123 (Thin Pyrex window for gamma rays).
[1]SHAND, E. B.: *Trans. Amer. Inst. Elec. Eng.* **60** (1941) 814–818 (Electrical breakdown strength of glass).
[2]SHAND, E. B. (Corning Glass Works): Curves for manufacture tolerances for borosilicate tubes reported by PHILIPS, C. J. (q.v.).
[3]SHAND, E. B. (Corning): *Glass Engineering Handbook*, 2nd. ed. (New York, 1958).
[1]SHAW, M. R.: *Trans. AMIEE* part II, **71** (Jan. 1953) 384–387 (Resistance welding of hard glass).
[2]SHAW, M. R.: *Elect. Eng.* **72** (1953) no. 1, pp. 31–34 (Electrical resistance welding of glass).
[3]SHAW, M. R.: US Pat. 2 470 376/1949 (Resistance welding glass by interrupted graphite coating).
SHERWOOD, R. G.: *J. Amer. Chem. Soc.* **40** (1918) 1645; *Phys. Rev.* **12** (1918) 448 (Gas released from glasses)

[1]SIEMENS U. HALSKE: DRP 391 232/1921/1924 (Dried tube-base).
[2]SIEMENS U. HALSKE: DRP 350 318/1920/1922 (Double-wall construction for discharge tubes to prevent puncture by static charges).
SIMON, H., and R. SUHRMANN: *Lichtelektrische Zellen u. ihre Anwendung* (Berlin, 1932).
SINGER, G.: *J. Res. Nat. Bur. Stds* **16** (1936) 233 (X-ray screening glasses with PbO and PbO + BaO).
[1]SLOSIAR, J.: *Spekané sklo ako materiál vákuovej techniky, jeho technológia a klasifikácia* (*Sinter Glass as Vacuum Material, its Technology and Classification*) (Thesis) (Bratislava, 1959).
[2]SLOSIAR, J.: *Sklář a keramik* **7** (1958) 79–82 (Classification proposal for sinter glass).
[1]SMELT, J.: *Philips Techn. Rdsch.* **2** (1937) 87–93 (The glassy state).
[2]SMELT, J.: *Verres et Réfractaires* **6** (1952) 75–82 (Glass for TV tubes).
SMID, J. *et al.*: *Měniče iontů, jejich vlastnosti a použití* (*Ion Exchangers, their Properties and Applications*) (Prague, 1954). **[10.7]**
SMITH, C. P. *et al.*: *RCA Rev.* (1958) 334–348 (Joining glass components of TV tubes with solder glass).
SMITH, P. L., and N. W. TAYLOR: *J. Amer. Ceram. Soc.* **23** (1940) 139 (He permeability of technical glasses).
SNYDER, C. L.: FIAT Final Report No. 278 (Solderable metalizing by Schoop-gun spraying Al and Cu onto hot glass).
SODER, R.: *Die Silicone* (Züricb, 1954).
SOLOMIN, N. V.: *Steklo i keramika* **7** (1950) no. 10, p. 14 (Basis for planning compositions of glasses).
[1]SPÄTE, F.: *Glastechn. Ber.* **10** (1932) 521 (Glasses for vacuum purposes).
[2]SPÄTE, F.: *Glastechn. Ber.* **2** (1924) 1; *idem* **4** (1926) 121 (Strains in glass).
[3]SPÄTE, F.: *Weiß-, Hohl- und Geräteglas* (Leipzig, 1931).
[4]SPÄTE, F. *et al.*: *Glastechn. Ber.* **12** (1934) 34 (Review of the transition temperature of glass).
[1]SPRINGER, L.: *Lehrbuch der Glastechnik*, 3rd ed. (Dresden, 1944).
[2]SPRINGER, L.: *Laboratoriumsbuch für die Glasindustrie* (Halle (Saale), 1950).
[1]STANWORTH, J. E.: *Physical Properties of Glass* (London, 1950).
[2]STANWORTH, J. E.: *Glass Rev.* **2** (1945) 5 (Intermediate glasses, Brit. Thomson-Houston Type C 42, C 43 and C 44, between Mo glass and ordinary sodium glasses).
[3]STANWORTH, J. E.: *J. Soc. Glass Techn.* **30** (1946) 381 (High-resistance phosphate glass).
[4]STANWORTH, J. E.: *J. Soc. Glass Techn.* **34** (1950) 153–172 (UV transparent glasses; including borate glasses).
[5]STANWORTH, J. E.: *J. Soc. Glass Techn.* **34** (1950) 5–9 (Pb-free Fe-sealing glasses).
[6]STANWORTH, J. E., and A. E. DALE: DRP 845 248/1949/1951 (Alkali-resistant sheathing glass for Kovar base glass).
[1]STEVELS, J. M.: *Progress in the Theory of the Properties of Glass* (New York, 1948).
[2]STEVELS, J. M.: *J. Soc. Glass Techn.* **34** (1950) 80–100; *Philips Res. Rep.* **5** (1950) 13; *idem* **6** (1951) 34 (Relation between dielectric loss and composition in glasses).
[3]STEVELS, J. M.: *Philips Techn. Rdsch.* **13** (1952) 385–396 (Dielectric loss in glass).
[4]STEVELS, J. M.: *Verres et Réfractaires* **5** (1951) 4 (Low-loss glasses containing Li).
[5]STEVELS, J. M.: *Glastechn. Ber.* **26** (1953) 227–231 ($\tan\delta$ of glasses for frequency 10^2 to 10^{14} c/s and $T =$ 0–600°; origin of losses).
[6]STEVELS, J. M.: *Verres et Réfractaires* **4** (1950) 3–9 (Sinter glass flat presses).
STEWART, A. B.: *Rev. Sci. Instr.* **21** (1950) 258 (Degassing glass by graphite coating and IR radiation).
STEYSKAL, H.: *Arbeitsverfahren u. Stoffkunde der Hochvakuumtechnik; Technologie der Elektronenröhren* (Mosbach/Baden 1955).
STOCKDALE, G. F., and F. V. TOOLEY: *J. Amer. Ceram. Soc.* **33** (1950) 11–16 (Changenin the transparency of glass by weathering).
STOOKEY, S. D.: *Ceramics from Glass*; Preprint of *Appl. Phys. Lab., Johns Hopkins University* (Baltimore, 1956).
[1]STRONG, J.: *Modern Physical Laboratory Practice* (London, 1944) pp. 151–187: metalizing glass surfaces).
[2]STRONG, J.: *Rev. Sci. Instr.* **6** (1935) 97 (Cleaning glass surfaces before metal evaporation by brushing with a highly ionized gas flame).
[3]STRONG, J.: *J. Phys. Rad.* **11** (1950) 451 (Cleaning processes for use in vacuum evaporation of metals).
[1]STRUTT, M. I. O., and A. VAN DER ZIEL: *Physica* **10** (1943) 445 ($\tan\delta$ of glasses as a function of temperature).
[2]STRUTT, M. I. O.: *Arch. Elektrotechn.* **25** (1931) 715–122 (Dielectric properties of various glasses as functions of temperature and frequency).

STUCKERT, L.: *Die Emailfabrikation*, 2nd ed. (Berlin, 1941).

[1]SUN, K. H.: *J. Soc. Glass Techn.* **31** (1947) 245–253 (Basic conditions for glass forming).

[2]SUN, L. L., and K. H. SUN: *Glass Ind.* **29** (1948) 686–691, 714, 716 (Glasses that absorb or transmit X-rays).

[3]SUN, K. H., and L. L. SUN: *Glass Ind.* **31** (1950) 507–515 (Neutron absorbing and transmitting glasses).

SYLVANIA ELECTRIC PRODUCTS INC., Electronics Div., New York 18 N. Y.: Techn. Inf. No. EC 21: Recording, dilatometer Type 135 (Fully-automatic, 1000° max., program controller, ink-recording, temp. axis 300 mm long, precision 0.2%).

SZYMANOWITZ, R.: *Glass Ind.* **26** (1945) 125–127, 151 (Graphite coatings on glass).

TAKAHASHI, K.: *J. Soc. Glass Techn.* **37** (1953) no. 175, *News and Reviews* (Calculation of thermal expansion coeffs.).

[11.7]

TAYLOR, W. C., and R. D. SMITH: *J. Amer. Ceram. Soc.* **19** (1936) 331 (Solubility of glasses in H_2O).

THIENE, H.: *Glas* (Jena, 1931; Michigan, 1944).

[1]THOMAS, M.: *Glastechn. Ber.* **4** (1926/27) 323 (Annealing glass).

[2]THOMAS, M. (Osram-Glaswerk Augsburg): private communication 1954 (Recent developments in Osram glasses).

TIELSCH, A., and K. ENDELL: *Glastechn. Ber.* **12** (1934) 84–87; see also *Silikattechnik* **5** (1954) 503, Fig. 2 (Viscosity measurements on molten glass with the rising-ball viscosimeter).

TODD, B. J.: *J. Appl. Phys.* **26** (1955) 1238–1243 (Water release of technical glasses at elevated temperatures, but below softening point).

TOOL, Q., and I. B. SAUNDERS: *J. Res. Nat. Bur. Stds* **40** (1948) 67–83 (Thermal expansions of Pyrex glass).

TRIER, W.: *Glastechn. Ber.* **27** (1954) no. 5, pp. 164–166 (Temperature and stress conditions in the cracking of glass).

TURNBULL, J. C.: *J. Amer. Ceram. Soc.* **33** (1950) 54–56 (Fully-electric recording dilatometer).

[1]TURNER, W. E., and F. WINKS: *J. Soc. Glass Techn.* **14** (1930) 84 (Expansion characteristics of strained glass).

[2]TURNER, W. E.: *J. Soc. Glass Techn.* **32** (1948) *News*, p. 73 (Melting glass in Pt-lined crucibles).

UHLMANN, W. E. M.: *Electronics* (Jan. 1955), pp. 161–163 (Construction of a storage tube with flat press and 27 current leads).

ULLMANN, F.: *Enzyklopädie der techn. Chemie*, 5th ed. (Vienna, 1930).

UMBLIA, E.: *Glass* (Oct. 1951), pp. 343–351; *Glasteknisk Tidskrift* **5** (1950) no. 6 (Metalizing glass).

UNGELENK, A.: Measurements on lead glass made by the "Deutschen Spiegelglas A.G.-Grünenplan" (information made available privately by courtesy of the author).

US GOVERNMENT: *Control of Radiation Hazards in the Atomic Energy Program* (Washington, 1950).

VESELOVSKIJ, S. F.: *Stekloduvnoje delo* (Moscow, 1952).

VIELHABER, L.: *Metalloberfläche* **1** (1947) 112–113 (Compositions of enamel); see also *Emailtechnik* (Berlin, 1939).

VIOLET, F. *et al.*: *Ann. Radioelectr.* **2** (1947) 24–74 (Glass in the radio tube industry).

[1]VOLF, M. B.: *Techniká skla* (*Technical Glass*) (Prague, 1953).

[2]VOLF, M. B.: *Tavení skla* (Prague 1952).

[3]VOLF, M. B.: *Sklář a keramik* **5** (1955) 90 (Composition of Czech glasses).

[4]VOLF, M. B.: *Sklářské rozhledy* (Prague) **26** (1950) no. 6/7 (Thermal shock resistance of glass).

[5]VOLF, M. B.: *Sklář a keramik* **6** (1956) 105–106 (New Czech hard apparatus-glass "Simax").

[6]VOLF, M. B.: *Tschechoslovakische Glasrevue* **13** (1958) no. 10, pp. 16–20 (Properties of Czech technical glasses).

VÚ SKLÁŘSKÝ, Hradec Králové, středisko Sázava: Composition and properties of Czech glasses (information kindly made available to the author).

WAGNER, K. W.: *Arch. Elektrotech.* **2** (1914) 371 (Electrical properties of composites).

WALSH, E. J.: *Bell Lab. Record* (May 1954) pp. 183–187 (Attaching 7 μ W grid-wires to Mo support rods by enamel instead of gold-braze).

[1]WARREN, B. E., and J. BISCOE: *J. Amer. Ceram. Soc.* **21** (1938) 259–265 (X-ray structure investigations on sodium silicate glass).

[2]WARREN, B. E.: *J. Amer. Ceram. Soc.* **24** (1941) 256 (Survey of work on arrangements of atoms in glass).

WARREN, H. G.: *Vacuum Symp. Trans.* 1954 (Comm. on Vac. Techn.) (Boston, Mass., 1955) (pp. 109–115: "in-line" exhaust principle).

WARTENBERG, H. von: *Z. Techn. Phys.* **13** (1932) 479–481 (Determination of transition temperature from maximum internal pressure withstood by glass tubing).
WEHNELT, A.: *Handfertigkeitspraktikum* (Braunschweig, 1920).
WEHNER, G. K.: *J. Appl. Phys.* **25** (1954) 270–271 (Mechanism of sputtering).
WEIGEL, R. G.: *Licht* **4** (1934) 1, 13, 39 (Opal glasses).
WEIN, S.: *Metal Finishing* **42** (1944) 534, 610, 669, 736 (Metalizing glass, ceramic, etc.).
WEINZETTL, V.: *Slabopr. obzor* **17** (1956) 566–573 (Automatic pumping systems).
[1]WEYL, W. A.: *J. Soc. Glass. Techn.* **33** (1949) 220–238 (Dielectric properties of glass as functions of composition).
[2]WEYL, W. A.: *J. Soc. Glass. Techn.* **30** (1946) 90–172 T (Solarization of glass).
[3]WEYL, W. A.: *J. Soc. Glass Techn.* **32** (1948) 247 (Effect of heavy metal ions on the surface properties of glass). **[10.7]**
[4]WEYL, W. A.: *Glass Ind.* (May/July 1947) pp. 231, 300, 349, 408 (Practical importance of the surface chemistry of glass).
WHEAT, W. N.: *Schott u. Genossen of Jena*, CIOS Report No. XXXIII-69.
WHITE, I. F., and W. B. SILVERMAN: *J. Amer. Ceram. Soc.* **38** (1950) 252–257 (Solarization of glass).
WHITNEY, W. E.: *The Gas World* **132** (Sept. 1950), pp. 342–343 (On the quality of city gas).
WILLIAMS, P. D.: *Phys. Rev.* **78** (1950) 353 (Mass-spectrographic analysis of gas released from technical glasses).
WILLOT, W. H.: *J. Soc. Glass Techn.* **34** (1950) 77–79 (Wear hardness).
WITTWER, H.: *Vakuumtechnik* **6** (1957) 111–112 (Method for determination of wall-thickness of glass tubing).
WOOD, E. M. S.: *Glass Ind.* (Jan. 1946) pp. 24, 46, 51 (Metalizing hot glass by spraying Al).
WOYTACEK, C.: *Lehrbuch der Glasbläserei* (Vienna, 1932).
WRIGHT, D. K.: US Pat. 2 148 314; 2 148 315; 2 194 373; 2 324 972 (Large floodlamps with front window sealed by fusion).
WYCKOFF, R. W. G.: *Electron Microscopy* (New York, 1949) (Includes shadow-casting evaporation of prepared specimens with heavy metals).
YARWOOD, J.: *High Vacuum Technique* (London, 1945) (esp. pp. 81–92; silvering glass); see also 3rd ed. in German, Berlin, 1955; English ed. 1956.
ZACHARIASEN, W. H.: *J. Amer. Chem. Soc.* **54** (1932) 3841–3851 (Atomic structure of glass).
ZIENER, TH.: *Glastechn. Ber.* **17** (1939) 329 (Propane-acetylene mixtures for glass-working, instead of city gas).
ZIMBER, R. M., and A. B. DUMONT: *Radio Eng.* **10** (1930) 31 (Electron tube manufacturing machines).
ZINKE, A., and H. NEUMÜLLER: DRP 761 322/1941/1953 (Lead borate solder glass).
ŽIŽKA, J., and J. BETKA: *Sklář a keramik* **6** (1956) 29–30 (Coating glass with silicone dry film).
ZSCHIMMER, E.: *Z. VDI* **39** (1923) 960 (Transition temperature of glass).
ZUNICK, M. I., and I. B. GOSLING: *Glass Ind.* **32** (1951) no. 3, pp. 117–120, 144 (Hard glasses for X-ray tubes).

CHAPTER 11

QUARTZ GLASS, QUARTZWARE AND VYCOR GLASS

(ALEXANDER-KATZ, GIALANELLA, GÜNTHER)

[11.1]

NOTE: *crystalline* quartz is rarely used in electron tubes; one exception is special photocell windows. When cementing this material, it must not be heated rapidly or too high, since at 573° it recrystallizes expands and fractures.

11.1. Manufacture of Quartz Glass and Quartzware

(SINGER)

Quartz glass used in vacuum tube construction generally consists of pure SiO_2 produced by melting naturally occurring crystalline material ("rock crystal"), whose main source is Brazil; it comes in sizes from that of a walnut to an egg, and costs 15–50 cents per lb. Quartz glass, like ordinary glass, may be considered as a supercooled fluid (cf. 10.1, especially Fig. B 10-1).

If the starting material is ordinary quartz sand, the result is an opaque, milky-white and slightly impure substance called quartzware, permeated with many small gas bubbles. This is because even at temperatures around 2000° the sand melt is not fluid enough for the bubbles to escape; yet if the temperature is raised, the evaporation of SiO_2 is too rapid. The porosity of ordinary commercial quartzware is about 3–4 v/o, the pore diameter (max.) 0.6 mm. There are often inclusions of C, at most 0.5% by weight, max. diameter 0.3 mm. Apart from bubbles and lower purity, quartzware does not differ in any basic physical or chemical properties from quartz glass.

The practical manufacture of quartzware tubing ([1]BOTTOMLEY, see also THOMSON, KUTSCHENREITER) proceeds as follows: a graphite or carbon rod, acting as tube core, is inserted in the middle of a rotating drum filled with pure quartz sand or, better still, granulated rock crystal of 0.5 mm grain-size; this is heated by passage of current (1000 A, 15 V) till the sand fuses to a pasty mass. After shutting off the current and removal of the core, a quartzware tube is left which does not adhere to the core because, apparently, the melt and core react to produce CO which holds the quartz away from the hot core rod (ASKENASY). If the tube is extracted from the furnace at not too low a temperature, it can be drawn or pressed (possibly in molds) without reheating, by blowing with compressed air ([2]BOTTOMLEY). The surface of the material when formed is usually fused to a smooth finish by oxyhydrogen flame.

There is a similar process for making quartzware tubes up to 300 mm dia., used by the HERAEUS Co. (see FORTEY). Washed, purified quartz sand is forced centrifugally against the inside of a high-speed rotating steel cylinder; at the same time, a carbon arc

140 A, 120 V, 50 mm length) is moved slowly along the cylinder axis so that the inside of the sand layer fuses to a quartzware cylinder. This is removed, after cooling, from the underlying sand, scraped clear of any sand adhering to the outside and finally ground to O.D. The same method can be used to make dishes, crucibles, beakers or any radially symmetrical shapes, with wall-thickness about 6 mm.

Tubes of clear fused quartz can be made by the following method tested on continuous production by HERAEUS-PLATINSCHMELZE (Hanau) (see GROSS). A ball of clear fused quartz (dia. *ca.* 50 mm) is fastened to the end of a quartzware tube about 1.2 m long and heated in an air furnace to about 1750°. It is then removed from the furnace by [11.1]

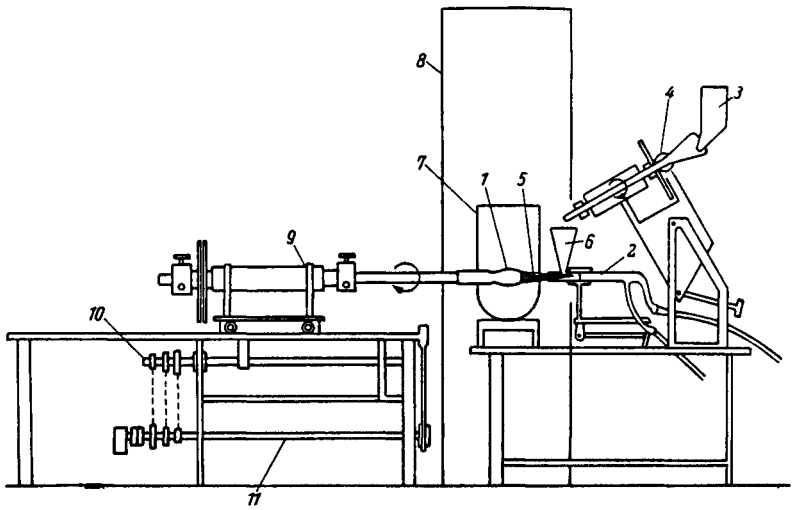


Fig. B 11-1 System for making optically clear quartz glass by the spray method (HERAEUS, Hanau) (see FORTEY, GROSS)

1 rotating quartz glass rod; *2* oxyhydrogen burner (see also Fig. B 11-1A); *3* hopper for rock crystal powder, 0.2–1 mm size; *4* device for feeding powder spray to the burner flame *5* through hopper *6*; *7* radiation screen (SiO_2 muffle); *8* extraction hood; *9* lathe; *10* change gears; *11* torque rod

the support tube and, still incandescent, rolled over a bed of rock crystal chips about 1–3 mm in size. If enough chips adhere to the soft quartz glass, it is returned to the furnace and reheated under rotation. By repeating this process the quartz-glass end grows to about 80 mm dia. and 500 mm length; from time to time a carbon rod is introduced into the heated quartz glass via the hollow support tube to prevent it fusing together. Then a length of about 150 mm at the end of the glass piece is heated to high temperature and drawn to tubing with a pair of tongs.

According to the SILICA SYNDICATE LTD., this process can be mechanized as follows: a horizontal quartz glass core-rod is arranged between the electrodes of a carbon arc, and is kept in oscillation along its axis while it rotates continuously. Rock crystal powder is poured continuously from above and fuses to the core. The arc may be replaced by a burner flame. This process, somewhat modified, was used successfully by HERAEUS (Hanau) to make optical-quality, pure quartz glass (see FORTY, GROSS), and Fig. B 11-1 shows the scheme. A quartz glass cylinder, 40–60 mm dia., turning at

200–300 r.p.m. is heated at one end to over 1750° by oxyhydrogen burner. A precision, continuous-feed device directs rock crystal powder (0.2–1 mm grain) from above into the burner flame, normal to its axis. The powder is heated to 2000° and thrown against the hot quartz cylinder and is fused on to it at about 250–150 g/hr without interruption, to form a bubble-free product. All parts of the spraying unit are made of fused quartz glass, including the burner plus hopper (Fig. B 11-1 A). The powder for the spray is made as follows: coarse sizings of rock crystal are washed in HF and distilled water, then dried. They are then heated in air to 800° and quenched in cold distilled water to [11.1] fragment them to small crystals, which are fine-ground in a special agate or steel mill.

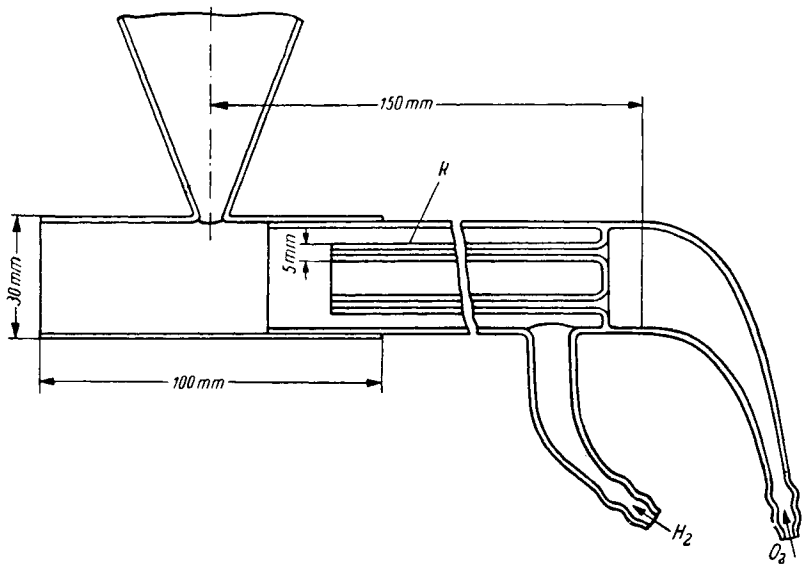


Fig. B 11-1 A Dimensional sketch of the H_2—O_2 burner with hopper (see Nos. *2* and *6* of Fig. B 11-1). Made exclusively of quartz glass; oxygen is fed through three separate tubes *R*

In the latter case, the crystals should be washed afterwards in HF and sieved through a magnetic iron sieve-separator. Small crystals below 0.2 mm are removed from the powder by a pneumatic method. For further details of the "spray" process for very pure quartz glass, see FORTEY, GROSS, LADOO.

According to WEITZ, clear quartz glass is made in the USA by the following method: chips of rock crystal are poured into a tubular, thin-walled graphite crucible and heated to softening point *in vacuo* in a high-temperature radiation furnace. When the crystals have been fused to a compact ingot, pressurized inert gas is fed into the furnace which is heated to higher temperature. The heater current is shut off, the melt is cooled and the graphite crucible then cracks because its α is much higher than that of quartz glass. The fragments of graphite are removed, the surface of the ingot freed from residual graphite with a grinding roll, and then ground to a smooth finish. The finish grinding can be carried out far quicker than for glass, and without coolant water-spray, because

the thermal shock resistance of quartz is greater. The process produces transparent, solid quartz cylinders of 25–470 mm dia., 100–200 mm long, which are generally worked up in the usual way in oxyhydrogen burner flames or in high-temperature furnaces with protective gas for the heater elements. Tubing is made by driving a pointed graphite rod through the center of the quartz cylinder ingot at high temperature (1800–1900°), a process that will produce uniform walls and O.D. up to 20 mm. Making larger diameter tubing by this method fails partly due to the difficulty of achieving an even, high temperature-distribution in the forming zone, and partly to the appearance of "harder" regions (SiC) with higher M.P. so that the tube comes out lumpy and uneven (LADOO). [11.1]

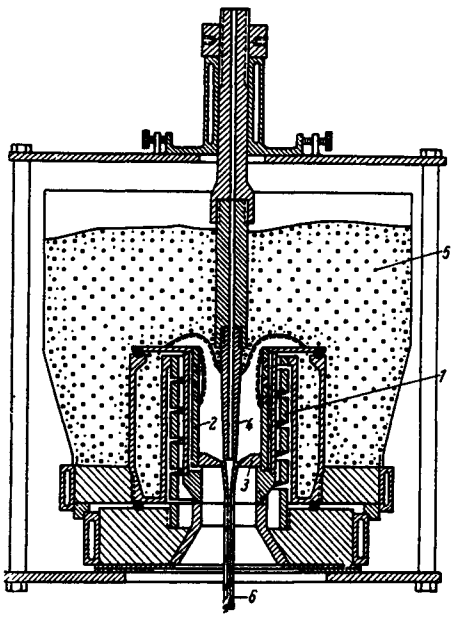


Fig. B 11-2 Melting and drawing furnace for clear quartz tubing, with heater, crucible, die and mandrel of carbon or graphite (S. A. DES MAN. DES GLACES)

1 heater coil; *2* crucible, filled with fused quartz; *3* draw-die; *4* mandrel for drawing, with central air channel; *5* unfused rock crystal chips; *6* quartz tube leaving the die nozzle

There has been no lack of attempts to make quartz tube and rod by equipment based on the DANNER drawing machine (Figs. B 10-106 and B 10-107). The chief difficulty is the high minimum temperature of 1900–2000° needed for proper drawing viscosity of the quartz (10^6 to $10^{5.5}$ P). Only graphite can withstand such temperatures without special gas protective atmospheres in closed vessels—and then only for short periods. Figure B 11-2 shows this kind of equipment; the powdered rock crystal is melted in a graphite crucible and heater coil, and the drawing mandrel and die are also graphite. The life of the equipment is obviously only short.

However, substitution of high-melting materials (W, Mo) for graphite and, therefore, protective gases especially in all parts of the apparatus attacked by air, enabled the equipment to be built successfully. The reliability and life are satisfactory, and fully-automatic production of clear quartz glass tube up to about 20 mm dia. is possible. (See HÄNLEIN, also FORTEY, GROSS.) Figure B 11-3 shows a schematic cross-section

through a melting plus tube-drawing device of this type, used mainly to make 8 mm I.D., 1 mm wall, clear tube for Hg lamps with quartz bulbs. About 72 W wire heaters (*1*), 1.7 mm dia., are clamped by rings and screws (*2* and *3*) at both ends to form the surface of a cylinder of about 150 mm dia.; the lower end is about 50 mm below the level of the draw-die orifice (*13*). The clamping rings are attached to two water-cooled current-feed caps (*4* and *5*). The upper cap (*4*) is rigidly connected to the water-cooled

[11.1]

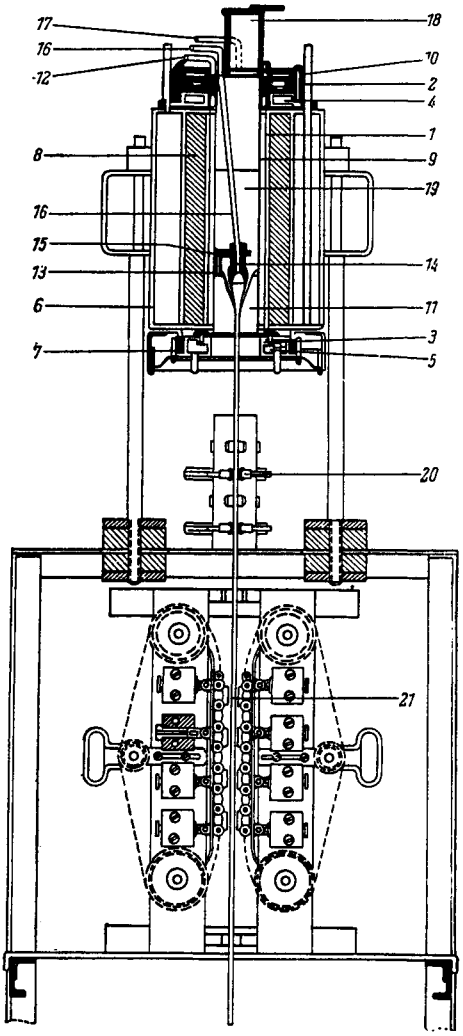


Fig. B 11-3 Automatic melting and drawing equipment for clear quartz glass tubing used by OSRAM (HÄNLEIN, see also GROSS). See Fig. B 11-3A for furnace construction

1 heater wires; *2* and *3* clamping rings; *4* and *5* water-cooled caps; *6* water-cooled furnace shell; *7* oil ring; *8* lagging; *9* crucible; *10* water-cooled support for crucible; *11* crucible extension; *12* protective gas inlet for heated volume; *13* die opening; *14* drawing mandrel; *15* support; *16* protective gas inlet for die; *17* protective gas inlet for crucible space; *18* crucible opening; *19* melt; *20* guide-rolls; *21* drawing unit

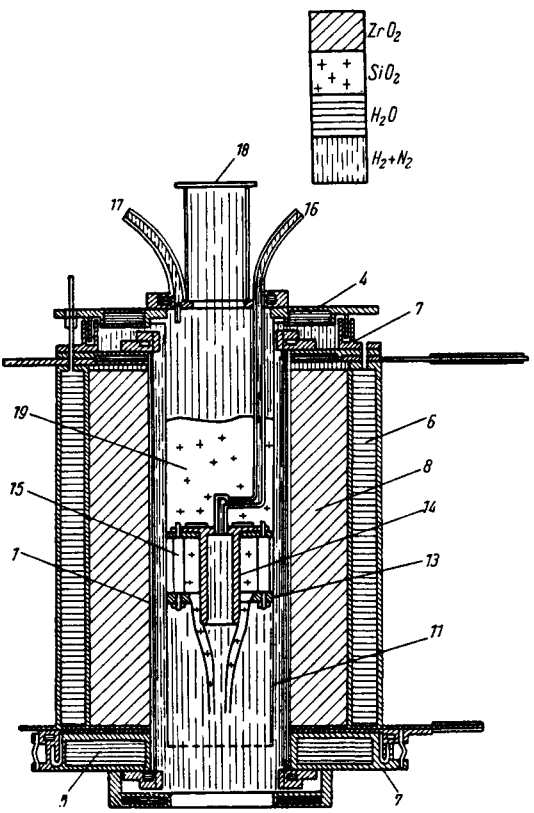


Fig. B 11-3A Furnace design for unit shown in Fig. B 11-3. Key as per B 11-3

furnace shell (*6*), of I.D. about 500 mm. The lower cap (*5*) has an outer oil-filled ring (*7*) in which is immersed a ring screwed to the shell (*6*); this enables the cap (*5*) that holds the heater wires (*1*) to maintain the furnace seal against atmospheric pressure while following the expansion of the wires, and so keep them taut. The heater system (*1*) is surrounded by a thermal insulator (*8*) 600 mm long, I.D. 170 mm, O.D. about 500 mm, made of compacted zirconia. Inside (*1*) there is a closed, cylindrical melting crucible (*9*), 400 mm long, 125 mm dia. and made of 0.5 mm Mo or W sheet, materials are not attacked by white-hot quartz at 2000° in the presence of forming gas ($H_2 + N_2$). This crucible is fastened at the top end to a water-cooled cap (*10*), and its lower end carries a [11.1] cylindrical extension (*11*) that projects below the level of clamping ring (*3*). In this way it is possible to keep the hot space round the crucible free of SiO_2 vapor and supply it with a separate non-flammable protective gas atmosphere of 80% N_2 + 20% H_2 (by volume) through inlet tube (*12*). In the floor of the crucible (*9*) lies the actual tube-drawing die, made by boring out solid refractory metal such as Mo. The circular opening (*13*) has inside it a cylindrical hollow mandrel (*14*) projecting downwards, with a bottom orifice; a support device (*15*) holds it exactly concentric with the exit funnel (see also Fig. B 11-3A). This forces the quartz glass streaming from the crucible opening to flow round the mandrel, spiral out of the funnel, and so take on the shape of a tube. To prevent the viscous tube collapsing to a solid rod, forming gas is fed into the upper hole in the mandrel from a special Mo tube (*16*). The crucible is also filled with forming gas via tube (*17*). The crucible charge is about 13 kg of rock crystal. The temperature cycle up to drawing point is about 2 hours. The crucible is recharged every 10 minutes or so through upper opening (*18*) with lumps of rock crystal the size of walnuts; the lumps are preheated in a special furnace to about 800° with a slow rise-time, and must then be rapidly transferred to the hot melting-furnace. If this is not done, the lumps split into small pieces when rapidly heated in the crucible past the transformation temperature (573°), and the quartz produced from the melt is extremely seedy due to the difficulty in fining mentioned earlier. The filling level of the melt at 2000° (*19*) is about three-quarters of the crucible height, and is tested by a Mo rod. When the still-soft quartz tube emerges from the die, it is fed first over the guide rolls (*20*) below the furnace to prevent kinking; when sufficiently cooled, and thus hard enough (about 30–40 cm below the die), it is gripped on both sides by asbestos-clad iron shoes (*21*) and drawn downwards without interruption. The dimensions of the tube depend chiefly on the draw-rate and the size of the quartz reservoir in the furnace, but less on the die size, so that with the same die the diameter of the tube can be set from 8 to 20 mm by controlling the draw-rate only. Below the drawing unit, the tube can be cut off continuously to length (about 60 cm). The output for 75 kW power consumption was about 20 m of tube per hour, 8 mm I.D., 1 mm wall. The furnace life was about 3 weeks, corresponding to 15,000 m of tubing. The cost price at the end of World War II ran to about 3–5 Marks at the value then obtaining.

It will be clear that practicable tolerances are much greater than those for ordinary glass stock, because of the difficult manufacturing process. For normal tube the I.D. tolerance is $\pm$5–7.5%, and $\pm$0.3 mm on machine-drawn tube diameters up to 12 mm.

Good-quality works quartz-glass made from rock crystal is at least 99.9% SiO_2. Table T 11–1 contains detailed analyses.

TABLE T 11-1. ANALYSIS OF QUARTZ AND VYCOR GLASSES

TYPE	CONTENT (w/o) OF:						
	SiO_2	B_2O_3	Al_2O_3	Fe_2O_3	Na_2O	K_2O	MgO
Russian-made quartz[1]	99.95	—	0.01	0.004	0.04	0.028	0.012
Vycor 7900[2]	96.3	2.9	(R_2O_3) 0.4	[5]	0.02	0.02	—
[11.2] Special, for resistance thermometers[3]	97.75	0.40	1.12		0.39		CaO 0.21
Silibor, similar to quartz[4] . . .							

(1) Made by LOMONOSSOV WORKS (USSR).
(2) Made by CORNING GLASS WORKS (USA).
(3) Made by unknown firm, analysis 1955.
(4) Made by VEB JENAER GLASWERK SCHOTT U. GEN., Jena; can be joined to ordinary quartz glass. Only supplied in plates 80 × 80 mm or disks 80 mm dia., 2 mm thick; small sizes up to 8 mm thick.
(5) Traces of As_2O_3.

11.2. Manufacture of Vycor Glass

(See Table T 10-4, Al, 7900, 7910, 7911, etc.)

In the last ten years, completely new methods have been employed successfully to make glasses whose SiO_2 content is so high (95% or more) that they can replace "true" 100% silica in many cases (HOOD, [1,2]NORDBERG, see also SMEKAL). These glasses were first marketed under the collective title of "Vycor brand" (CORNING trade name); they are made in the following four stages (HOOD):

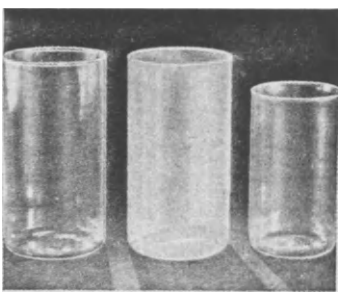
(a) The starting material is a "base" glass whose composition is approximately 75% SiO_2, 20% B_2O_3, and 5% alkali oxides, with α (20–300°) = 36×10^{-7} 1/°C. It is fused in the usual way in a tank furnace to make a homogeneous product, and can be blown like ordinary hard glass to desired shape: tube, bulbs, etc. (see Fig. B 11-3 B, I).

(b) The basic glass now undergoes about 5 hr heat-treatment at 600–650°; at this temperature there is no deformation, and no devitrification in this period of time. The components separate into two non-crystalline, glassy phases. This occurs even at lower temperatures but then requires longer completion times, e.g. 3 days at 525°. At temperatures above 650°, the two phases are no longer spongy or porous, but take on drop-like structures so that subsequent separation by leaching (see below) is impossible.

One phase is almost solely B_2O_3 and alkali oxides, therefore soluble in acid. The other is predominantly a porous but coherent silica sponge skeleton, virtually insoluble in HCl. The separation shows up by a light opalescence, and under certain conditions as opal clouding.

(c) The dehomogenized material is leached at 98° in 3-normal HCl or 5-normal H_2SO_4 until practically nothing is left but SiO_2 skeleton. However, the basic glass has been blown, and heat-treated for several hours, so that volatile B_2O_3 and Na_2O have been partly evaporated from the surface which is now silica-rich; this means that the surface

is relatively resistant to leaching. It is therefore recommended that the glass is first superficially etched with dilute HF (HOOD), or "polished" with a fine grinding powder (VOLF), but no surface mechanical damage must occur since this would lead to cracking in the subsequent leaching process. After this, the basic glass is wiped with cotton batting moistened with alcohol or ether, placed for a short time in a dilute, slightly warmed solution of Na_2CO_3 and then washed in hot water. Now follows the actual leaching process. The top layers of glass, the first to be leached, swell due to filling of the pores with aqueous acid solution; this puts the inner layers under dangerous tensile stresses that can lead to fracture during the leaching. Addition of 20% KCl to the acid, or use [11.2] of acid saturated with ammonium chloride considerably reduces the swelling and hence the danger of cracking, apparently because the water concentration, and therefore its absorption by the silica sponge, is reduced. The leaching process lasts rather a long time; 1 mm wall-thickness requires at least 1 day. For this reason, thick-walled Vycor



I II III

Fig. B 11-3B Manufacturing process for Vycor ware, from 95–96% SiO_2

I blown basic glass
II the same piece after dehomogenizing and acid-leaching
III the same after sintering at about 1000° (³CORNING)

(>8 mm) is not made from solid basic glass but from leached powder glass, especially that produced from fragments cracked off during leaching (see above). The powder is worked up by the methods of ceramic manufacture (molding or slip-casting), dried, and sintered at only 1200–1300° (cf. 10.6.IV). In spite of the relatively low manufacturing temperature, these products of the "multiform process" can have any desired wall-thickness and are the same as fused quartz glass in all properties except their opacity. SiO_2 powder is used in a similar process (KITAJGORODSKIJ), where it is sintered with sodium borosilicate glass and then leached.

After acid treatment, the glass is carefully washed by immersion in pure *running* water of all the leached surfaces for 12 hr. This is to remove all traces of the dissolved phase and of impurities, such as Fe, which may be introduced by leaching. The final product has the same external shape as before the leaching process. When wet, it is almost opaque, after drying, diffuse opaque (see Fig. B 11-3B, II) with bluish opalescence; it is often brownish-colored due to absorption of impurities from the surroundings. It is fairly strong but sensitive to thermal shock. Since it is highly absorbent, it should not be handled with bare fingers; all impurities should be kept away, especially if a high UV transparency and low $\tan\delta$ of Vycor made from this material is of any importance.

Leached material of this type is sold commercially as glass filters under the name "Vycor Brand No. 7930", made by CORNING Glass Works; see also THOMSON. It has an

apparent density of 1.45 g/cm³. Its pores are very small, most of them between 20 and 40 Å (see SCHWERTZ). Leached Vycor porous glass can be used as a virus and bacteria filter since the latter have a cross-section of 1–2 μ (10,000–20,000 Å) and virus cells 0.02–0.25 μ (200–2500 Å). The permeability of a 2 mm thickness of porous glass 7930 for water at 35° and at 700 Torr gauge is 6.1×10^{-4} cm³/cm²-hr. For acetone under the same conditions, the value is 17.1×10^{-4} (NORDBERG, SCHWERTZ). For 1 atm gauge of O_2 or H_2, the values are 4 and 19 cm³ (NTP)/cm²-hr. Since the porosity is about 30 v/o, the glass will absorb about 25 w/o H_2O. Even in a desiccator at 20° over
[11.3] P_2O_5, it still holds about 5 w/o H_2O. The high porosity implies an enormous surface area, about 120–200 m²/g, so that the material has large absorptivity, and can be used as a catalyst.

(d) After leaching, the SiO_2 skeleton is slowly dried, by gradually bringing it up to a few hundred degrees, to avoid damage by bursts of water vapor. The temperature is then raised to 900–1000° and held for a short time. The porous skeleton sinters, shrinking linearly in all dimensions by 14% to form a pore-free, fully-glass body (Fig. B 11-3B, III) that at the end of the process is transparent in wall-thicknesses of a few mm, but light opaque white in appearance for greater wall-thicknesses (NORDBERG, SHAVER). It is possible to raise the temperatures to 1200° during the sintering process but the piece must be supported to avoid deformation by softening. When the glass transformation process is over, the body can be cooled rapidly, and can even be quenched in cold water without cracking since it consists of more than 95% fused quartz at this point (Table T 11–1). Working up therefore differs very little from that of "true" SiO_2 (see 11.3).

If stress is laid on the highest possible UV transmission, then after careful drying of the porous glass up to 600°, further slow heating to 900° is carried out in a reducing, hydrogen atmosphere, e.g. a flow of 92% N_2 + 8% H_2. Immediately after shutting off gas flow and evacuation of the furnace, actual sintering is done in vacuum, preferably at 1000° for $^1/_2$ hr and then at temperatures up to 1200°. In this way, not only are traces of Fe_2O_3 (strong UV absorber) converted to FeO, but residual As_2O_3 is evaporated off; As_2O_3 has been shown by experience to increase the tendency of the sinter glass to form bubbles when worked in the flame ([2]NORDBERG).

11.3. Working Fused Silica

Since quartz only begins to become plastic above 1500° ($\eta = 10^9$ P), it must be worked either by oxyhydrogen burner (Table T 10–20, last row) or in the electric arc between carbon electrodes, magnetically "blown" to the shape of a pointed flame (see, e.g., GABOR, SINGER, Fig. B 9.3-15). The working temperature lies between 1800° and 2000° ($\eta = 10^{6.5}$ to $10^{5.5}$ P, cf. Fig. B 11-4). At these temperatures, evaporation is rapid, the VP is about 10 Torr at 1800°, 100 Torr at 2000° (see Fig. B 11-5B). On health grounds (silicosis hazard) these vapors must be removed by suction through an extraction line facing the direction from which the flames from the burner are coming. The vapor condenses on the inner wall of the line as a flaky white dust, as one can easily prove for oneself. The high operating temperature also entails the use of dark protective glasses to avoid conjunctivitis and other eye damage. Apart from these simple but essential precautions, quartz is easier to work than glass since the low α and therefore high thermal shock resistance of quartz enable it to withstand rapid, large thermal

changes without fracture; small incandescent quartz pieces can be water-quenched, for example. However, flame-working must be preceded by careful surface cleaning with ethanol or methanol since traces of hand-sweat (mostly CaO) and dust attack quartz when heated to redness ("corrosion") and also reduce UV transmission.

For vacuum tube purposes, *quartzware* must be fused to a smooth finish at least superficially by means of the burner, otherwise its porosity makes it hard to degas. But even with quartz glass tube drawn new from the works, it is often recommended that the tube surface be fused over in the oxyhydrogen burner flame to remove any longitudinal capillaries. The simplest way to degas quartz glass vacuum tubes after first pumping is to play a broad-flame from a hand-torch over the tube for 1 min and then repeat. One should start at the lead-throughs and work to the exhaust stem and then [11.3]

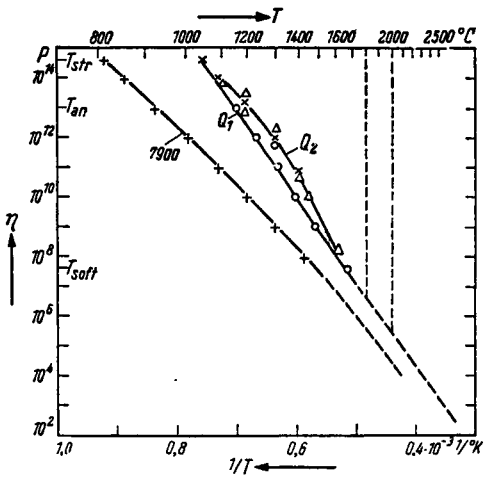


Fig. B 11-4 Viscosity η of pure quartz compared with Vycor (CORNING 7900, 96% SiO_2) plotted as temperature (T °C) functions and functions of $1/T$ (°K)

Q_1 CORNING data for quartz; Q_2 quartz data from VOLAROVICH (cf. also Fig. B 10-15)

to the quartz pumping line. The quartz can be allowed to reach 1000° if the electrodes permit. After this initial degassing, the final process is generally carried out in a drop-over electric furnace with the surface temperature of the quartz glass at 600°; in the case of gas discharge lamps, this is best done while a powerful discharge is maintained in the tube.

If quartz glass is heated over 1000° for several hours it devitrifies, that is it converts from the amorphous state to crystalline structure. On cooling, the devitrified parts go milky and clouded once the quartz is below 230°. (Local milkiness of surface during flame-working can occur between the soft, heated zone and nearby cooler regions; this is just condensation of sublimed SiO_2, harmless except to the appearance of the material.) Devitrified and non-devitrified material have different αs, and so stresses can arise which lead to fracture. Short, repeated excursions to 2000° in general produce no danger of devitrification, but the inner surfaces of water-cooled, highly-rated, high-pressure gas-discharge lamps with quartz bulbs show devitrification during their life (*ca.* 100 hours). Small cracks develop at the inner surface and finally spread so far that the tube fractures, quite apart from the fact that the intensity of radiation of such lamps is

always gradually reduced, 30% or more by the end of their life. Since impurities act as crystallization nuclei, quartzware usually devitrifies more readily than quartz glass, which is much purer.

Quartz glass can be drawn out to very thin fibers (down to 1.5 μ dia.), which exhibit great tensile strength (see Fig. B 11-5) and therefore are excellently suited to making micro-balances, for example. These balances may be used for absorption measurements

[11.3]

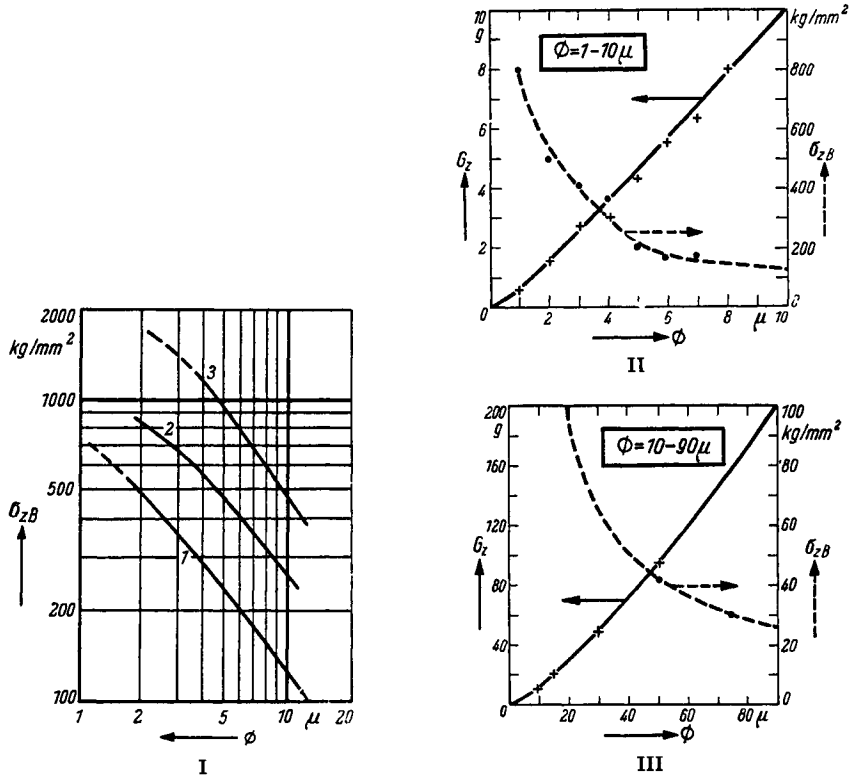


Fig. B 11-5 Fracture load G_z and tensile strength σ_{zB} of hot-drawn quartz fibers as functions of fiber diameter

I { 1 in ordinary moist air; 2 in air dried with $CaCl_2$; 3 in vacuum, after baking out (SCHURKOW) }

II, III in ordinary air (REINKOBER)

in vacuo. Details of manufacture of fibers will be found in STRONG (p. 195) and ANGERER (p. 116). Quartz glass can only be joined (by fusion) to ordinary silicate glasses by use of intermediate glass, since the expansions are different. To fuse quartz to hard-glass envelopes (Fig. B 11-19) at least five intermediates are normally required, and about ten for sealing to soft glass. Data for corresponding intermediates will be found in Tables T 10–2, D 9 and E 3, and T 10–4, D 8, D 9, E 3. For sealing W lead-throughs of 3 mm dia. into quartz tubes, industry only uses one intermediate glass, for example Type WQ 31 of the GEC, Wembley, England (Table T 10–2, E 3). For further details see Chapter 31, Quartz-Metal Seals.

Quartz glass, unlike glass, cannot be scratched and then broken; however, it can be drilled, ground and polished with SiC; thin, medium-hard, high-speed carborundum wheels (2500–5000 r.p.m.) will grind it or cut it. The carborundum tool must run very smoothly and must not chatter; a powerful water jet must be used to cool the cutting zone during the operation. Quartz can also be cut off with rubber slitting wheels loaded at the edge with diamond grit.

11.4. Vycor Working

[11.5]

For thermoplastic working of Vycor, there are two quite distinct processes, corresponding to the methods of manufacture:

One way is to shape the base glass (see 11.2) by the well-known methods of working hard glass, allowing for later shrinkage in sintering, and then convert by leaching and sintering to 95% SiO_2 as described above. This is a good method for mass-production of simple objects (Fig. B 11-3B).

The other way is restricted to thermoplastic forming of the many finished and commercially available products in Vycor — tubing, envelopes, disks, rods. This is the preferred method for one-off, precision, and complex devices, and differs little from the working of 100% silica glass; as Vycor's viscosity is somewhat lower (Fig. B 11-4), small objects can be worked using ordinary city gas + O_2 (Table T 10–20, penultimate row), but large pieces have to be worked with $H_2 + O_2$.

Below 900°, Vycor has little tendency to devitrify, but above 1000° the effect is marked and up to 1200° Vycor is more devitrifiable than quartz; at still higher temperatures however, the rate is never as high as that observed for quartz between 1300° and 1500°. As with silica, the process involves formation of crystobalite crystals; it spreads from the surface inwards and is first visible on cooling Vycor to below 300° where the surface quite suddenly takes on the appearance of frosted or etched glass. This change is due to conversion of β-crystobalite to α-phase material in the range 200–275°, the surface being thereby disrupted.

Surface clouding, as with silica, can be caused by condensation of evaporated SiO_2 round the fusion zone during working. It can be removed with dibite HF. Bubbles can form in Vycor if worked at too high a temperature by torch-flame (KREIDL).

Vycor 7900 can be fused directly to 7900 Multiform Vycor and to normal silica; intermediates of proper α, of course, have to be used to join Vycor to ordinary technical glasses.

11.5. Physical Properties of Quartz Glass (Fused Silica)

(see, e.g., SOSMAN, WATSON)

The chief properties are collected in Table T 11–2 supplemented by Figs. B 11-4 to B 11-11A. The properties of quartzware and Vycor 7900 are included.

Fused silica has a series of properties unlike those of any other material. Its α is exceptionally small (Table T 11–3; Figs. B 11-5A, B 10-34), the transition temperature and softening point are very high (Fig. B 11-4). This makes sealing to metal extremely difficult, and virtually only foil seals of plastic Mo or Ta are possible (Chapter 31). On

TABLE T 11–2. PROPERTIES OF QUARTZ GLASS, QUARTZWARE AND VYCOR 7900 (>95% SiO_2)

			QUARTZ GLASS AND QUARTZWARE			VYCOR[12] 7900
Density		g/cm³	2.0–2.3 (2.1–2.2)			2.18 [2.15][10]
Mohs' hardness		—	(5–) 7			
Tr. T. T_g	$\eta = 10^{12.3}$ P	°C	1100–1120[1]		Fig. B 11-4 and Fig. B 10-15	(900)
T_{str}	$10^{14.6}$ P	°C	1050[1]	1020[3]		820[6]
[11.5] T_{anneal}	10^{13} P	°C	1150[1]	1120[3]		910[6]
T_{soft}	$10^{7.6}$ P	°C	1655[1]	1650[9]		1500[6]
Working range	10^{6}– $10^{5.6}$ P	°C	1900–2000[1]			(1600–1700)[6]
T_{work}	10^{4} P	°C	2300 (extrap.)[1]			(2000)[6]
Max. operating temp.	continuous	°C	1000			900
	transient	°C	1300			1200 [1300][12]
Vapor pressure		Torr	1000 °C: ~ 10^{-5} 1220 °C: ~ 10^{-2}		Fig. B 11-5B	
Tensile strength		kg/mm²	7–12[11] fibers see Fig. B 11-5		quartzware: 4.5	Similar to CORNING's Pyrex 7740 see Table T 10–4, A 1
Compress. strength		kg/mm²	160–200		quartzware: 35	
Bend strength		kg/mm²	7			
Torsion strength		kg/mm²	3			
Young's modulus		kg/mm²	6200–7200			
Torsion modulus		kg/mm²	2400–3150			
Poisson's ratio		—	0.17; (0.14)[15]			0.18
Average thermal expansion coeff.[3]		10^{-7} 1/°C	20–300 °C: 6.27 20–1000 °C: 5.40	see Table T 11–3, Fig. B 10-34, Fig. B 11-5A	quartzware: 0–300 °C: 6.9 0–1000 °C: 5.0–5.2	0–300 °C: 7.5 [8][10] [7] Fig. B 11-5A
Thermal hysteresis		1/°C	$\frac{\Delta l}{l} \times \frac{1}{T_2 - T_1}$: (−1 to −5) × 10^{-9}			
Specific heat		$\frac{cal}{g\ °C}$	100 °C : 0.20 500 °C : 0.27 1000 °C : 0.29			
Average specific heat		$\frac{cal}{g\ °C}$	0–100 °C : 0.1845 0–500 °C : 0.2302 0–900 °C : 0.2512			
Thermal shock resistance (TWB)		°C	Wall-thickness d = 3 mm: >1250 °C			d = 3 mm : 1250 6 mm : 1000 12 mm : 750
Thermal conductivity		$\frac{cal}{cm\ sec\ °C}$	20 °C : 0.0035 950 °C : 0.0064[4] see Fig. B 10-43		0.0026[4] 650 °C : 0.0065[14] see Fig. B 11-5c	
Electrical resistivity		Ω - cm	20 °C : 10^{17}–10^{18} 250 °C : $10^{12.3}$ 350 °C : $10^{10.5}$	see Fig. B 11-6 B 10-49 B 10-52 B 10-53		25 °C : 10^{17} 250 °C : [$10^{9.7}$] ($10^{11.2}$) < $10^{11.7}$ >[10] 350 °C : [$10^{8.1}$] ($10^{9.2}$) < $10^{9.6}$ >[10] Fig. B 11-6 and Fig. B 10-49, also Table T 10–4, A1
			Na content (w/o): 2×10^{-6}; 4×10^{-2} ϱ at 350 °C Ω - cm: 10^{12}; ≈10^{9}		OWEN; see Fig. B 11-6A	
$T_{x\ 100}$-point		°C	600			360
Surface resistivity		Ω	relative humidity: 60% : 3×10^{10}; 90% : 2×10^{9}		Fig. B 11-7	

TABLE T 11–2 *(continued)*

		QUARTZ GLASS AND QUARTZWARE		VYCOR[15] 7900
Electrical breakdown strength (thin plates)	kV/cm	20 °C : 250–400 500 °C : 40–50	Quartzware: 20 °C : 150–200 500 °C : 20–30	
Dielectric loss angle $\tan\delta$	10^{-4}	10^6 c/s: *ca.* 2 see Fig. B 13-10 10^{10} c/s: 1.7 see Table T 10–4, A1, footnote 33, Figs. B 10-70, B 11-7A, B 12-26, B 12-30 to B 12-32	Quartzware: 2×10^6 c/s: 6.7 5×10^7 c/s: 27 see also Fig. B 13-10	10^6 c/s: 6 10^{10} c/s: 9.4 see Figs. B 11-7A, B 11-7B [6]
Dielectric constant ε	—	10^6–10^{10} c/s: 3.78; see also Figs. B 10-65, B 11-7A, Figs. B 12-25 to B 12-26, B 13-10		10^2–10^7 c/s: 3.85
		25 °C, 60% relative humidity, 10^6 c/s: 4.4		10^{10} c/s: 3.82[6] see also Fig. B 11-7A
Total emissivity	%	Fig. B 12-68		—
UV transmission	%	Limit: 1200–1800 Å, 3000 Å: 98% see Figs. B 10-89, B 10-94, B 11-8		Limit: 1900–2000 Å; Figs. B 11-8, B 10-94, B 10-95
IR transmission	%	see Figs. B 11-10, B 10-83		see Figs. B 11-10, B 10-87
Radiant energy transmission (500–2300 °C)	%	—		see Fig. B 10-87
Gas permeability	$\frac{cm^3\ (NTP)\cdot mm}{sec\cdot cm^2\cdot Torr}$	see Figs. B 11-11, B 10-82A, B 10-82D, and Table T 11–4		For H_2 see RUSSELL, also Table T 11–4
Refractive index	—	18 °C, 5893 Å: 1.45859		1.45860

[11.5]

(1) From CORNING, see also Fig. B 10-15.
(2) REIMANN, page 223.
(3) According to heat-treatment, α can vary by 20% (DOUGLAS). Further measurements see EBERT, SOUDER.
(4) SEEMANN.
(5) For further data see Table T 10–4, A 1, type Vycor 7900–7911; for glass type 7900 see also footnote 33 to Table T 10–4, A 1; also Figs. B 10-70, B 10-72.
(6) Further data see Table T 10–4, 7900–7911, and glass type 7900 see footnote 33, Table T 10–4, A1, also Figs. B 10-65 and B 10-67.
(7) See also SOUDER.
(8) Cf. Fig. B 11-4, Table T 10–4, A1. Bracketed values are extrapolated.
(9) [1]NORDBERG.
(10) Values in [ ] brackets for Vycor 7900 Multiform, from [1]NORDBERG; in ( ) parentheses, for Vycor 7910, in < > for Vycor 7911 ([2]CORNING).
(11) Tensiles for quartz glass increase somewhat at elevated temps. For H.P. lamps, allowing for gradual onset of devitrification of internal surface, the safe loading ≈ 2.8 kg/mm².
(12) There are four Vycor brands available $\gtrsim 96\%$ SiO_2: (a) 7900, (b) 7910: UV trans. at 254; (c) 7911: Sun Lamp Vycor; (d) 7912: UV trans. at 185. All four have almost the same properties, except for UV limit (see Fig. B 11-8), given in Table T 10–4, A1, and this table.
(13) Bracketed values for special Vycor 7913 ([2]CORNING).
(14) KINGERY.
(15) GIALANELLA.

the other hand, the low α ensures a very high thermal shock resistance. This is assisted by good thermal conductivity which is higher than that of silicate glass (Figs. B 10-43, B 11-5c).

Chapter 10 has already dealt fully with the structure of silica and its consequences, i.e. low electrical conductivity and loss angle. The electrical resistance of silica is higher than that of the best glasses (Figs. B 11-6 and B 11-6A, but also Figs. B 10-49, B 10-52 and B 10-53). This has special advantages for hot-cathode construction with radiation-heated insulator bridges that run at high temperature (cf. Fig. B 11-12). In addition, the

TABLE T 11-3. AVERAGE LINEAR THERMAL EXPANSION COEFFICIENT ($\alpha_{20}\ldots_T$) OF FUSED SILICA[1]

TEMP. RANGE °C — °C	$\alpha_{20\ldots T}$[2] 10^{-7}/°C	$\alpha_{20\ldots T}$[3] 10^{-7}/°C	TEMP. RANGE °C — °C	$\alpha_{20\ldots T}$[2] 10^{-7}/°C	$\alpha_{20\ldots T}$[3] 10^{-7}/°C
20–100	5.10	5.3	20–600	6.00	6.0
20–200	5.85	6.0	20–700	5.71	
20–300	6.27	6.4	20–800	5.62	
20–400	6.35	6.5	20–900	5.56	
20–500	6.12	6.2	20–1000	5.40	0–1000 °C: 5.8[4]

[11.5]

(1) When measuring expansion coeffs. of solid materials with a differential dilatometer, using silica as a standard, these numbers should be added to the coeff. obtained from the expansion characteristics.
(2) Measured at 2 °C/min temperature rise on a test-rod from the LEITZ Co.
(3) EBERT.
(4) REIMANN.

surface conductivity of silica is at least a power of ten lower than that of hard glasses, although for the external parts of tubes it is moisture-dependent (Fig. B 11-7).

The dielectric loss (see paragraph above) is less, even at elevated temperatures, than any other known insulator except mica and rutile (Figs. B 10-70, B 11-7A; Table T 10–4, A1, footnote 33). The loss angle of *quartzware* is about a power of ten higher.

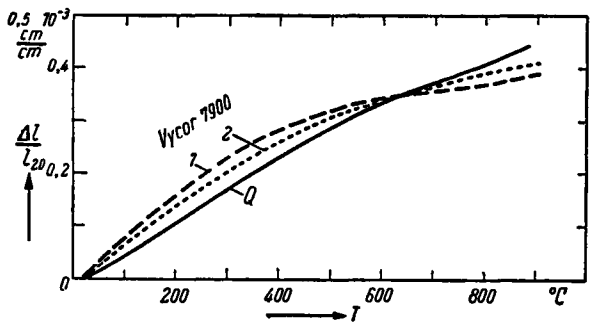


Fig. B 11-5A Expansion characteristics of fused silica (*Q*) and Vycor glasses 7900 and 7910
1 from SAUNDERS; *2* from LILLIE

UV transmission (Figs. B 11-8, B 10-89 and B 10-94) is the largest for all materials used in vacuum work. To clarify the technical, therapeutic and hygienic importance of UV (mostly produced artificially by quartz-envelope discharge lamps), Fig. B 11-8A gives the effects of various UV spectra in the form of curves, and also the chief ranges of application (see also KOELLER). The difference between silica and ordinary glass is demonstrated by Fig. B 11-9 for the case of the spectrum of a low-pressure Hg lamp. Good-quality silica still satisfactorily transmits wavelengths down to 1800 Å. For this reason, protective goggles should be worn when pumping and testing operational gas-discharge lamps, especially those with Hg-vapor filling, since UV causes conjunctivitis to an extent which increases with shortness of wavelength (cf. Fig. B 11-9A, which

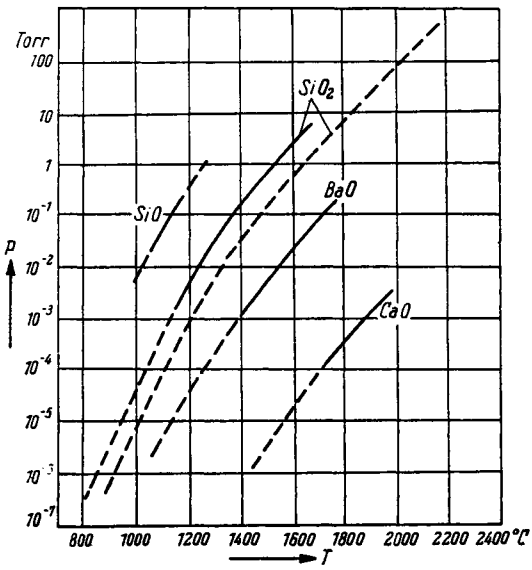
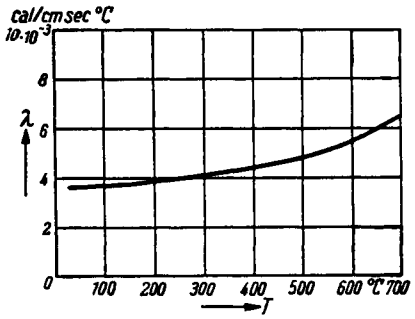


Fig. B 11-5B Saturation vapor pressure p of SiO_2 compared with SiO and some other oxides, expressed as functions of temperature T

Solid curves for SiO_2 from RUFF, dashed curves from earlier measurements; curve for SiO from SCHÄFER



[11.5]

Fig. B 11-5C Thermal conductivity λ of clear fused silica as a function of temperature T (KINGERY); cf. however, Fig. B 10-43, curve *1*

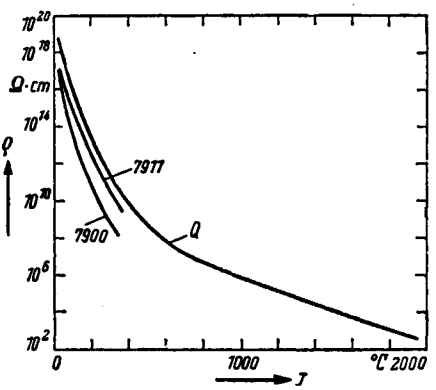


Fig. B 11-6 Electrical resistivity ϱ of silica glass (Q) compared with CORNING Vycor 7900 and 7911, as functions of temperature T

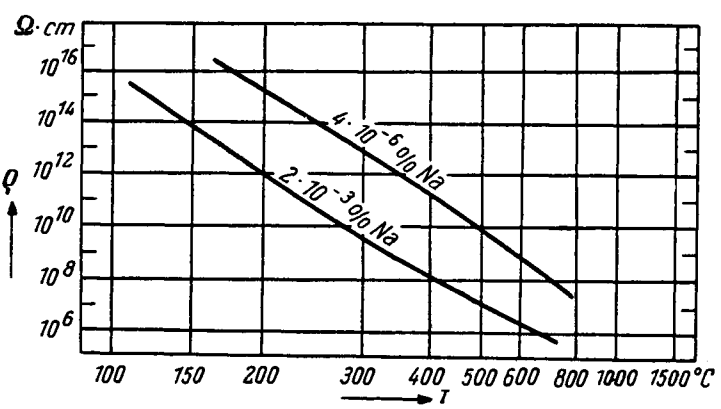


Fig. B 11-6A Resistivity ϱ of silica glass with various trace amounts of Na, as a function of temperature T (OWEN, see also COHEN, SEEMANN, STRAUSS, TAYLOR)

[11.5]

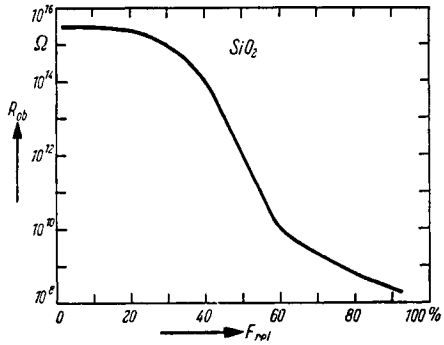


Fig. B 11-7 Electrical surface-resistivity R_{ob} of fused silica at 20° as a function of relative humidity F_{rel} of the surrounding atmosphere (GUYER)

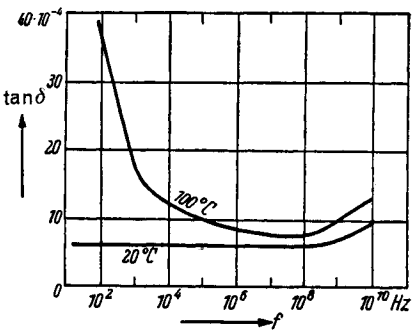


Fig. B 11-7B Dielectric loss factor tanδ of Vycor glass 7900 at 20° and 100° as functions of frequency f (see also Table T 10–4, A 1, footnote 33); for pure SiO_2 see also Fig. B 10-70

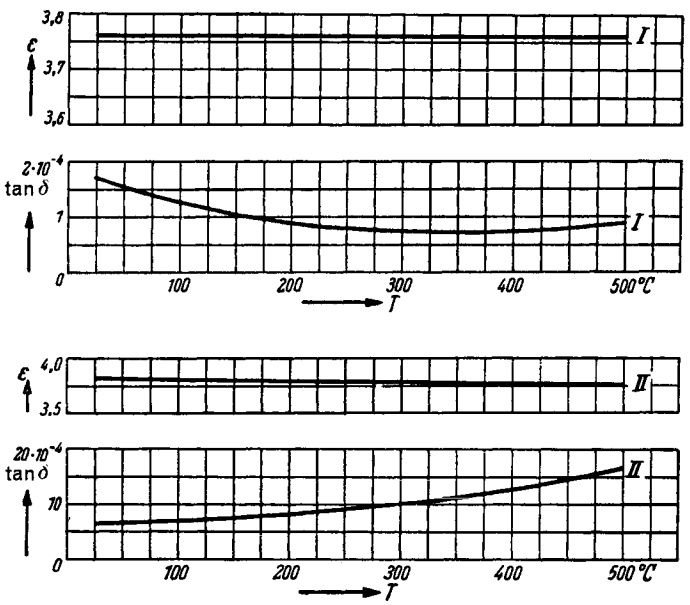
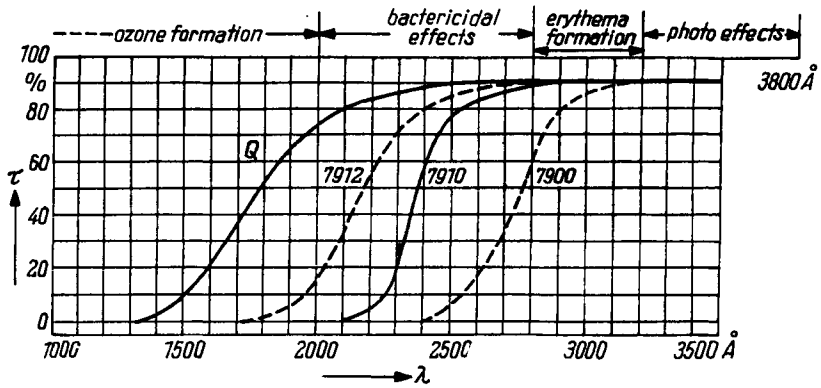


Fig. B 11-7A Dielectric constant ε and loss angle tanδ at 10^{10} c/s as functions of temperature T (HIPPEL)
I pure quartz glass (CORNING fused silica 915 C)
II Vycor glass 96% SiO_2 (CORNING 7911)

shows other biological effects of UV). Attenuation of UV by solarization (see 10.2.XVI) is relatively low with silica glass. See MOHN for some recent silica made by HERAEUS-QUARZSCHMELZE (Hanau), strongly absorbent below 2300 Å and therefore not ozone-forming.

In the IR, as in the UV, silica glass has the highest transmission (Fig. B 11-10). Up to 3.6 μ it is almost fully transparent. Thereafter the transmission falls off, becoming very poor at 5 μ. There are absorption bands at 3.3 and 4.3 μ.



[11.5]

Fig. B 11-8 UV transmission τ of pure silica glass (Q) and CORNING Vycor 7910 of 2 mm wall-thickness, as functions of wavelength λ (NORDBERG, see also FISCHER)

Dashed curve: Vycor 7912, 1 mm thickness (WEITZ); *dotted curve:* Vycor 7900, 1 mm wall-thickness (BERAN), see also Fig. B 10-95

Since reflexion loss amounts to 8%, the transmission is 92% maximum if there are no absorption losses. See Fig. B 11-8A for explanation of the importance of τ of fused silica

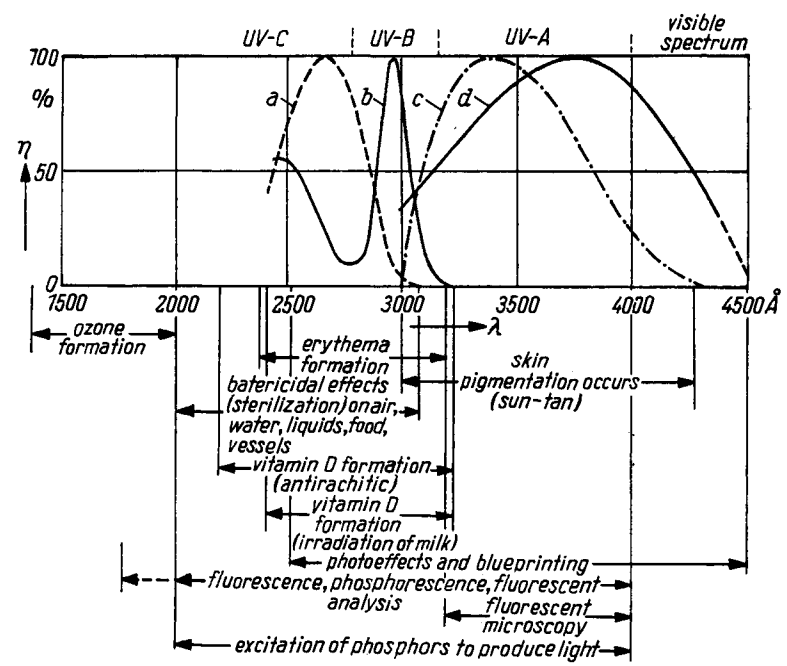


Fig. B 11-8A Efficiency η and range of application of UV radiation (KERN's data)

a bactericidal effects; *b* erythema curve; *c* skin pigmentation (sun-tan effect); *d* photochemical sensitivity curve of blueprinting paper (approx.)

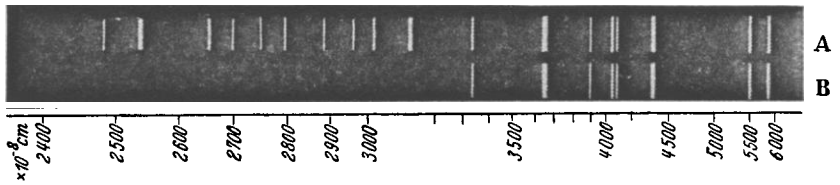


Fig. B 11-9 UV transmission of fused silica compared with that of ordinary silicate glass
A spectrum of light from low-pressure Hg lamp with SiO_2 envelope; *B idem* with glass envelope

[11.5]

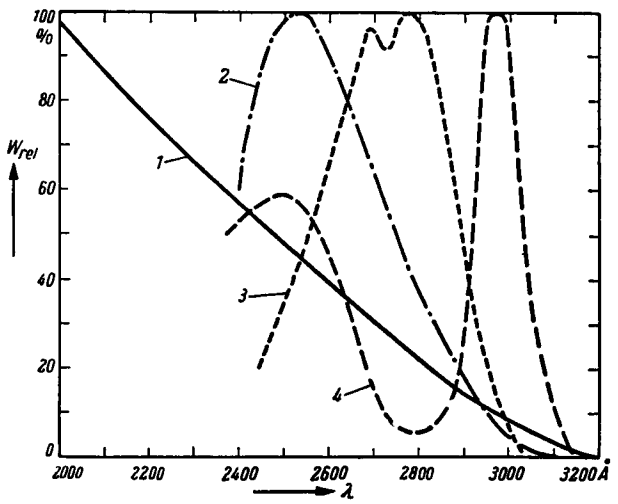


Fig. B 11-9A Relative values W_{rel} of biological effects of monochromatic UV of equal intensity as functions of wavelength λ (D'ANS-LAX); cf. also Fig. B 11-8A
1 production of conjunctivitis; *2* bactericidal effects on bact. coli; *3* absorption curve of unirradiated ergosterin (vitamin D_2 formation); *4* production of erythema: skin reddening after 1–6 hr followed by tanning

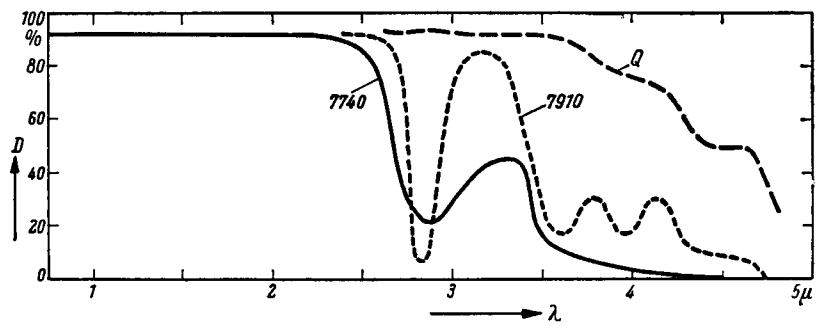
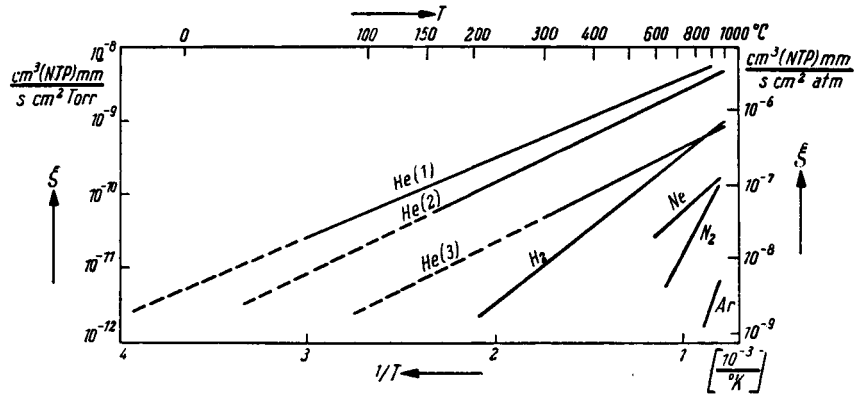


Fig. B 11-10 IR transmission *D* of pure fused silica 1 mm thick (*Q*) and of 2 mm Vycor 7910 (96% SiO_2) compared with 2 mm Pyrex glass 7740 as functions of wavelength λ (PHILIPS, see also FRITZ-SCHMIDT)

At high temperatures, silica glass is permeable to gases (BARRER, BAUKLOH, JOSSEN, NORTON, TSAI), in fact more so than ordinary silicate glasses (Figs. B 10-82A, B 10-82D). The He permeability at 180° is already noticeable, and besides He, permeability to other



[11.5]

Fig. B 11-11 Permeability ξ of fused silica to various gases, as functions of temperature T (°C) and of $1/T$ (°K). Cf. Fig. B 10-82D

Refs. He (1): NORTON; He (2): BARRER; H_2: BARRER; Ar: BARRER; N_2: J. JOHNSON; Ne: TSAI

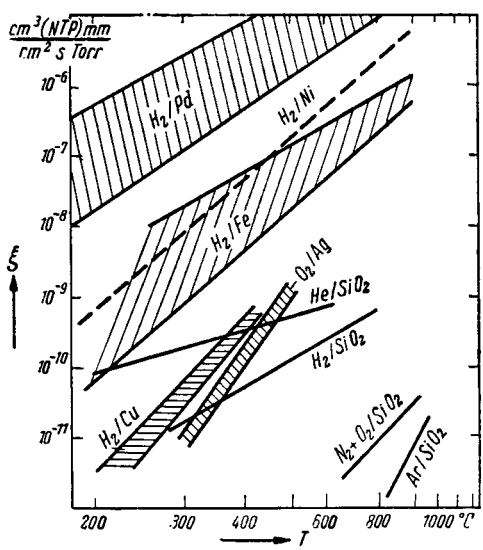


Fig. B 11-11A Comparison of permeability of SiO_2 glass with that of metals (cf. also Figs. B 9.5-8, B 11-11)

gases is detectable—H_2 (above 300°), Ne, N_2, O_2 and Ar (over 900–1000°) in descending order (Table T 11–4). Permeability is proportional to pressure gradient and for thin specimens inversely proportional to thickness. Temperature dependence (°K) is given by

$$\xi = A e^{-E/RT} \quad \text{or} \quad \log \xi = \log A - B/T,$$

TABLE T 11-4. GAS PERMEABILITY ξ OF FUSED SILICA AT VARIOUS TEMPERATURES T FOR VARIOUS GASES

[11.5]

T	ξ { ordinary numbers in units of 10^{-10} cm³ (NTP) mm/sec-cm²-Torr; italicized numbers in units of 10^{-7} cm³ (NTP) mm/sec-cm²-atm								
°C	He[1]	He[2]	Ne[1]	H_2[2]	D_2[4]	O_2[4]	Ar[3]	N_2[3]	N_2[6]
150	0.73 *0.56*	—							
200	1.39 *1.06*	—		0.022 *0.017*					
300	3.15 *2.4*	0.48 *0.32*		0.099 *0.075*					
400	6.15 *4.6*	0.99 *0.75*		0.37 *0.28*					
500	10.4 *7.9*	1.72 *1.3*	0.14 *0.11*	1.25[4] *0.95*					
600	16.4 *12.5*	3.0 *2.3*	0.28 *0.21*	1.43 *1.08*	1.7 *1.3*	<0.1 *<0.07*		0.065[7] *0.05*	0.066[7] *0.05*
700	21.9 *16.6*	4.25 *3.2*	0.42[4] *0.38*	2.52 | 2.1[4] *1.9* | *1.6*				0.132[8] *0.10*	0.146[9] *0.11*
800	28.5 *21.7*	5.5 *4.2*	0.81 *0.62*	4.25 *3.2*		Apparently less than for N_2	0.016[3] *0.012*	0.43 *0.33*	0.39 *0.30*
900	36.2 *27.7*	6.7 *5.1*	1.18 *0.9*	6.4 *4.9*			0.58[6] *0.44*	1.19 *0.90*	0.95 *0.72*
930	42[5] *32*	—	1.58[5] *1.2*	—			0.062[2] *0.047*		1.44[10] *1.10*
1000	45.4 *34.6*	8.4 *6.4*	1.63 *1.24*	10.0 *7.6*		(11)			
Atom-dia	1.95 Å	1.95 Å	2.4 Å	2.5 Å	2.55 Å	3.15 Å	3.2 Å	3.4 Å	3.4 Å

(1) TSAI, (2) BARRER, (3) BARRER, at 850 °C, (4) NORTON, (5) JOSSEN, (6) J. JOHNSON, (7) At 650°C, (8) At 750 °C: 0.268 (*0.204*), (9) At 750 °C: 0.271 (*0.21*), (10) At 950 °C, (11) According to NORTON, permeability at 700 °C for Ar, O_2 and N_2 should be less than 10^{-16} cm³ (NTP) mm / cm²-Torr-sec.

where E (cal) is the activation energy, R (cal/deg) the gas constant, A and B are constants (see also Figs. B 11-11 and B 11-11A). As E has different values at low and high temperature, one can deduce that high-temperature diffusion occurs through the

unoccupied sites in the silica lattice, and at low-temperature also along the intercrystalline cleavages (BARRER). After prolonged heating at over 1000° (i.e. after devitrification has begun), gas permeability usually rises, noticeably so with H_2 (BAUKLOH).

The gas permeability of silica has certain technical consequences: when degassing (heating) quartz-envelope vacuum tubes, the final stage should not take place in gas-fired furnaces or with gas burners but in an electric furnace. For the same reason exhaust-stem seal-off should be carried out by carbon arc (Fig. B 9.3-15). This is obligatory for sealing Ta foil to quartz (cf. GABOR, and Chapter 31). The high He permeability can, on the other hand, be used to introduce small amounts of He (see Fig. B 4.2-4); a [11.6] quartz finger is sealed to the apparatus via a series of intermediate glasses. The finger is surrounded with or filled with He and heated to about 900° by a heater coil wound round it.

11.6. Physical Properties of Vycor Glasses

(NORDBERG)

The properties of these glasses are given in the right-hand columns of Tables T 11–2 and in T 10–4, A1, types 7900–7912. In many cases, they are almost the same as those of 100% fused silica (quartz glass) but often the traces of B_2O_3 and alkali oxides have noticeable effects. The thermal expansion coefficient is little different from that of pure silica, and the thermal shock resistance is therefore large. The shape of the expansion curve is not, however, the same as that of pure silica (SOUDER). Electrical resistivity is not so extremely high as that of silica, but is only a little less especially in the high-ohmic Vycors like 7911 (see Fig. B 11-6). The same applies to the dielectric loss angle (Figs. B 10-70 and B 11-7B) and dielectric constant (Fig. B 10-65). These glasses have exceptional transparency: UV transmission of 7900 is high up to wavelengths no shorter than 3000 Å, the transmission for 2537 Å (Hg line) being only 10% at 2 mm thickness. However, the transmission in the UV of special glasses made for UV work, Vycor 7910 and 7911, is still excellent at 2536 Å; 2 mm thickness material is guaranteed by the manufacturer to have a minimum of 70% at this wavelength and is usually much better (Figs. B 11-8 and B 10-95). At 2100 Å, even Vycor 7910 is opaque, unlike fused silica, but there are special Vycors (e.g. 7912) which still transmit quite well at these wavelengths.

Solarization (loss of UV transmission by effects of prolonged exposure to UV) is low for 7910, just as for fused silica (Figs. B 10-94 and B 10-95): when 2 mm thickness of 7910 was UV-irradiated by quartz lamp (500 W) for 100 hr, the transmission loss was 6% average, max. 9% at 2536 Å; more prolonged irradiation produced no further solarization. The same Vycor was blackened (see 10.2.XVI) and after 2000 hr lost about 13% transmission, measured again at 2356 Å.

IR transmission of 7900 and 7912 are almost equal and not so high as that of pure fused silica because of absorption bands (Fig. B 11-10).

H_2 permeability of Vycor glass is about the same as that of pure fused silica in the range 700–975° (RUSSELL, see Fig. B 10-82D).

TABLE T 11-5. CHEMICAL BEHAVIOR OF FUSED SILICA (≧ 99.8% SiO_2)

REAGENT	REACTION
Metals[1]	
Ag	No attack
Al	Rapid attack at 700–800°
C	Reduction at 1050°
Ca	In vacuum, up to dull red heat: none
Cd	No effect; attack by vapor-phase material at elevated temps. over long periods
[11.6] Hg	None, up to very high temps.
Li	None up to 250°
Mg	Rapid attack at 700–800°
Mn	Attack only at high temps. in H_2
Na	Attack by vapor-phase material at high temps.
P	Reaction
Pt	Attack at high temps. in H_2
S	No appreciable attack
Sn	None
Zn	None
Metallic oxides[1]	
BaO	Slight attack at 900°
CaO	Attack at 1000°
CuO	Attack above 960°
Fe oxides	None up to 960°
MgO	No appreciable attack
Acids	
H_2O (even at 100°)	Virtually none
H_2SO_4	None
HNO_3	None
HCl (20°)	None
HCl (5%, 100°)	6 hr: 0.0005 mg/cm² loss
HF	Attack at all temps.
Phosphoric acid (> 300°)	Strong attack, though not so strong as on glass/ceramics
Organic acids	None
Alkaline solutions	
NH_4OH (10%, 20°)	48 hr: 0.009 mg/cm² loss
NaOH (1%, 20°)	240 hr on quartzware: 0.075 mg/cm²
NaOH (10%, 18°)	48 hr: 0.0045 mg/cm²
NaOH (2 N, 100°)	3 hr: 0.37 mg/cm²
NaOH (5%, 100°)	6 hr: 0.90 mg/cm²
KOH (1%, 20°)	240 hr on quartzware: 0.046 mg/cm²
KOH (30%, 18°)	48 hr: 0.013 mg/cm²
KOH (2 N, 100°)	3 hr: 0.34 mg/cm²
Soda (Na_2CO_3) (1 N, 18°)	336 hr: 0.0045 mg/cm²
Soda (Na_2CO_3) (2 N, 100°)	3 hr: 0.11 mg/cm²
$Ba(OH)_2$ (saturated, 18°)	336 hr: no weight loss
Na_2HPO_4 (saturated, 18°)	336 hr: no loss
Gases	
Cl, even hot and wet	None
HCl, SO_2	None

[1] Data from BERLINER QUARZSCHMELZE.

11.7. Chemical Properties of Fused Silica (Quartz Glass)

Fused silica is extremely inert, and in particular, and in contrast to ordinary silicate glasses, is not attacked by (neutral) water at 100°. It merely forms a water film whose thickness at 80% humidity was found to be about 0.45×10^{-6} cm, and at 90% about 2.7×10^{-6} (BRIGGS); on the other hand PARKS reported 13×10^{-6} cm film thickness in equilibrium with saturated water vapor. Since the water molecule has a diameter of about 3×10^{-8} cm, the values at high humidity corresponded to about 100–400 molecular layers. Pure fused silica is not attacked even by H_2SO_4 or HCl, but it reacts with HF, phosphoric acid, alkalis and alkaline salts, especially at high temperatures. It also reacts with electropositive molten metals and is attacked by hot metal oxides to form silicates. See Table T 11–5 for further details. [11.9]

Fused silica is not attacked by Hg or its vapor, but it is discolored by positive ion absorption from low-pressure Hg discharges in small-bore tubing. After penetrating the silica wall, these ions are neutralized and cannot escape again, or only to a small extent, because of their large atomic diameter. Hg in silica glass can be detected chemically. This effect is less for high-pressure discharges because the discharge is pinched (away from the wall).

The best way of cleaning contaminated silica tubes is to use 15% aqueous HF, aged by prolonged action on pieces of glass added to the liquid. Cleaned silica should then be placed for at least 1 hr in several changes of boiling distilled water or residual HF in capillaries will strongly attack the tube electrodes.

11.8. Chemical Properties of Vycor Glass

The behavior of Vycor is almost that of pure fused silica because of the high silica content of Vycor. It is attacked much less than ordinary technical glasses even by HF. It is very stable in the presence of H_2O (see Table T 10–15B) and of neutral or acid solutions (Table T 10–17A). It is attacked by alkaline solutions but less so than the so-called chemically resistant technical glasses (see Tables T 11–5A, T 10–16A).

11.9. Technical Applications of Fused Silica and Quartzware

Fused silica is sold as tube 1–200 mm I.D., wall 0.5–8 mm, and as rod and plate.

As shown by a rough comparison (Table T 11–6) with other glasses, quartz is recommended primarily for cases where the following properties are necessary: high temperature resistance, high electrical resistivity even at elevated temperatures, low dielectric loss, high UV transmission, and considerable resistance to corrosion (low sensitivity to weathering); above all, high price must be of no great consequence.

The annual production of technical glasses in the USA amounts to several million tons, but of quartz about 100 tons (WEITZ).

The following examples of the use of silica in vacuum technology should be mentioned:

(a) Piece-parts for construction, in HV; especially H.F. transmitter tubes. This is mainly for areas subjected to high temperatures (see Fig. B 11-12).

TABLE T 11-5 A. BEHAVIOR OF VYCOR 7900 (> 96% SiO_2)[1]; SEE ALSO TABLE T 11-5

REAGENT	REACTION
Cr, 1150°	2 hr in vacuum: none
Cu, molten	In vacuum: none
Ni, 1150°	2 hr in vacuum: none
Pb, molten	In vacuum: none
HCl (5%, 100°)	24 hr, 0.0005 mg/cm² weight loss (1)
NaOH (5%, 100°)	6 hr, 0.90 mg/cm² (2)
[11.9] Na_2CO_3 (N/50, 100°)	6 hr, 0.07 mg/cm² (3)
Distilled water	0.00303 w/o (4) weight loss
Gases	
Air (850°)	1 hr: no weight change
Cl	Inert
HCl	No attack even at elevated temps.
SO_2	No attack even at elevated temps.

(1) Compare Pyrex 7740: 0.0045 mg/cm², see also Table T 10-17 A.
(2) Compare Pyrex 7740: 1.4 mg/cm², see also Table T 10-16 A.
(3) Compare Pyrex 7740: 0.12 mg/cm², see also Table T 10-16 A.
(4) Compare Pyrex 7740: 0.0025 w/o, see also Table T 10-15 B.

(b) Envelopes for high-power, radiation-cooled transmitter tubes. These have the advantage over hard glasses of permitting degassing temperatures above 800° during evacuation, very important for medium-power tubes with gas-sensitive WTh cathodes. If electrodes are made of refractory metals (e.g. plates of Mo or Ta with sintered Zr powder coatings), considerable amounts of power can be radiated without water-cooling. Figure B 11-13 shows two commercially available tubes, for power outputs up to 10 kW (e.g. Type TYS 5–3000, made by MULLARD, England). The current leads are usually 3 mm dia. W rods sealed in with an intermediate glass (Type WQ 31, see Tables T10–2, E3, T10–4, E3). These tubes can be repaired at

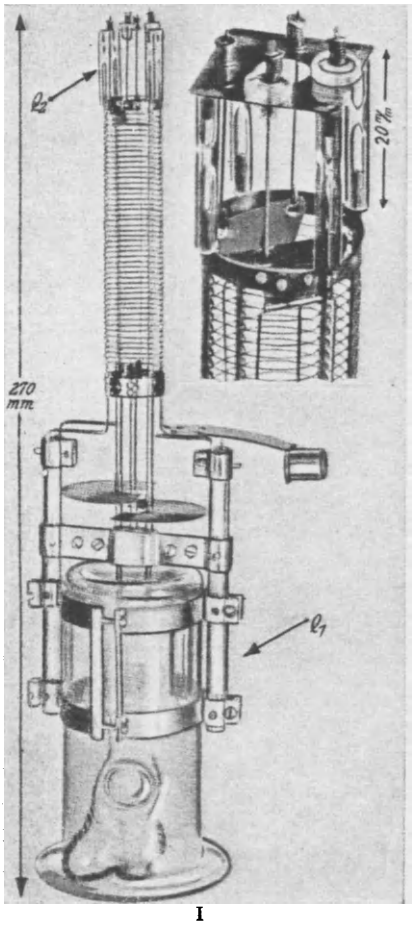
TABLE T 11-6. QUALITATIVE COMPARISON OF PROPERTIES OF FUSED SILICA WITH THOSE OF TECHNICAL GLASSES

	FUSED SILICA	96% SiO_2 GLASS	BOROSILICATE GLASS	LEAD GLASS	SODA-LIME GLASS
Price	Very high	High	Average	Low	Cheapest
Weight	Lightest	Light	Average	Heaviest	Heavy
Strength	Greatest	High	Good	Low	Low
Surface hardness	Best	Good	Good	Low	Medium
Hot-workability	Very poor	Poor	Average	Very good	Good
Heat resistance	Highest	Very high	High	Low	Good
Thermal shock resistance	Highest	High	Good	Low	Low
Elect. resistance	Highest	High	High	Very high	Medium
Dielectric loss	Very low	Very low	Average (1)	Low	High
Chemical inertness	Greatest	Large	Good	Medium	Low
UV transmission	Very good	Good	Medium	Low	Low

(1) Special glasses: low.

the end of their life as many times as desired, in fact at 60% of the cost of a new tube, and with the same life, according to the manufacturer.

(c) Tubes and envelopes (bulbs) of UV lamps for therapy, photography (printing) and other special purposes (see also BOURNE).



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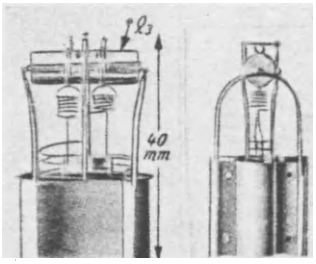


II

[11.9]

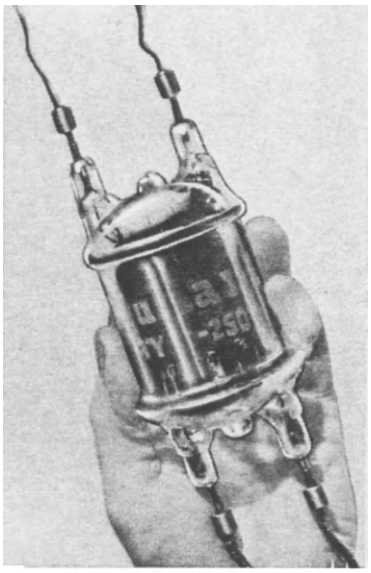
Fig. B 11-12 Example of electrode construction using quartz piece-parts

I cathode-grid system of short-wave transmitting tube (6 m): Q_1 silica rod for supporting grid; Q_2 section of silica tubing for insulating cathode tensioning (see right upper illustration for magnified view)
II upper section of small transmitting tube, shown front and side: Q_3 silica tube bridge to hold cathode spring and provide support for grid by, and insulate it from, the plate

1. Low-pressure therapy lamps with liquid cathodes (older type of UV sun-lamp), and with tilt-striking (Fig. B 11-14), operating at 100–1000 Torr, corresponding to cathode temperatures of 260–390°.

2. 13–60 W low-pressure germicidal lamps, fused silica bulbs, 40–90 mm long (see, e.g., Fig. B 20-63A) working at a fraction of a Torr Hg pressure (about blood-heat in operation, at the surface of the discharge section); about 90% of the energy emitted at 2540 Å.

3. Hg lamps with internal high-pressure burner, and a thermally insulating outer bulb coated with phosphor (see Figs. B 11-14A, B 11-14B, B 15-90, B 20-65 and B 20-67).



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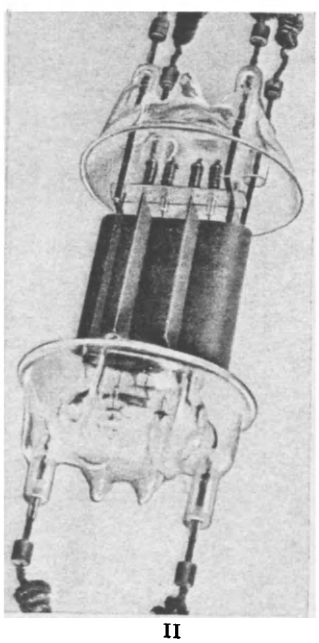

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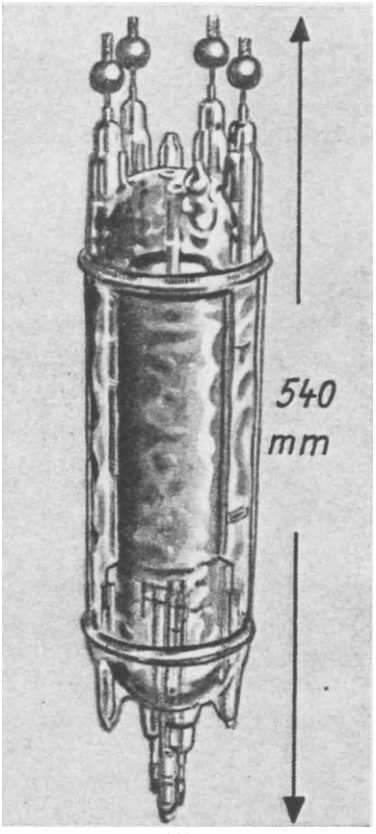


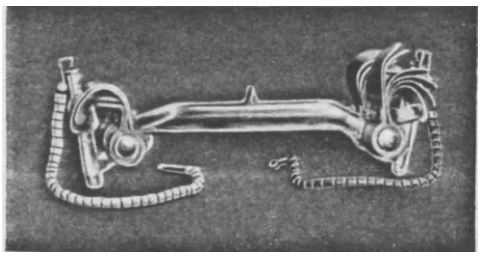
III

Fig. B 11-13 Silica envelope transmitter tube (courtesy of MULLARD ELECTRONIC PRODUCTS LTD., England) (cf. also MANNERS)

I TYS 2-250, for 550 W power output at 7.5×10^7 c/s
II same tube before sealing to the envelope
III TYS 5-3000, for 6300 W at 2×10^7 c/s, and 9100 W at 4.5×10^5 c/s, overall length 540 mm

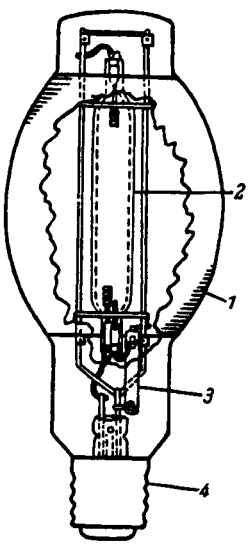
4. Quartz lamps mainly for therapy, with self-heating oxide cathodes, 2 Torr of Ar firing gas, and Hg droplets (operating pressure of Hg 1–5 atm), as shown in Figs. B 11-15 and B 11-15A; envelopes: cylindrical U-shapes or straight, O.D. 10–25 mm, tube length 10–30 cm, wall 1–1.5 mm approx.

5. High-pressure discharge lamps of high intensity (up to 100,000 stilb) with internal pressures up to 100 atm and far higher specific rating of the bulb than for ordinary Hg lamps (further details see BOURNE, FREEMAN, MANNERS, THOURET). The maximum permissible rating for the internal surfaces of lamps enclosed by a second glass jacket



[11.9]

Fig. B 11-14 Low-pressure quartz lamp with liquid cathode and tilt-striking for D.C. operation (so-called sun-lamp) (made by QUARZLAMPEN-GES., Hanau)



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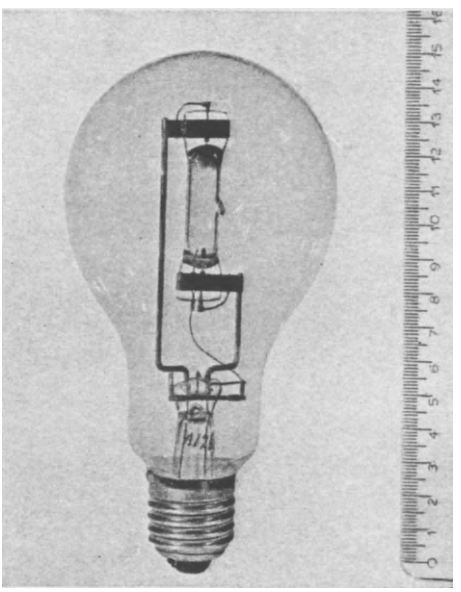


II

Fig. B 11-14A Hg lamps, with internal H.P. discharge lamp unit; cf. also Figs. B 15-90 and B 20-65

I design of type 3-H 1: efficiency 45 lumens/W, life 4000–6000 hr (ANON.). *1* outer evacuated envelope made of glass coated internally with phosphor; *2* internal Hg-vapor lamp with two self-heating electrodes and a firing electrode; *3* current-limiting resistor; *4* external connecting base

II a so-called MP lamp without phosphor (internal frosting omitted) 35–40 lumens/W, striking voltage *ca.* 180. Outer envelope filled with about 500 Torr N_2. Operating pressure of Hg in the small quartz discharge tube 5 atm or more (courtesy of PHILIPS, see also OUWELTJES)

is 10–15 W/cm², and for lamps running in free air with pure convection cooling, 20–45 W/cm², for the case of forced draught cooling, 50 W/cm² and more, and for globe lamps up to 150 W/cm² is possible, where the temperature at the coolest zone is 600–800° (corresponding to a pressure of 20–100 atm Hg); see Table T 11–7, which also gives the required wall-thicknesses for quartz lamps with globe or pear-shaped bulbs. Even a

500–800 W/cm² rating is possible for water-cooled, quartz-capillary, very high-pressure lamps (Hg at 70–100 atm).

It is of importance in manufacture of these high-pressure lamps that the wall-thickness is as nearly uniform as possible, especially at regions of high curvature and at corners. During pumping and testing, the lamps should operate behind protective glass

[11.9]

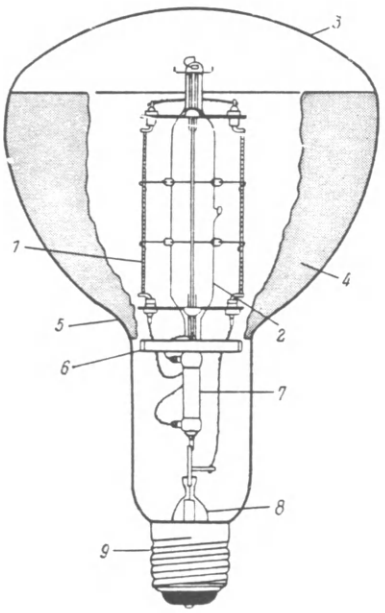
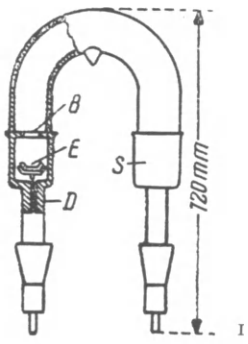
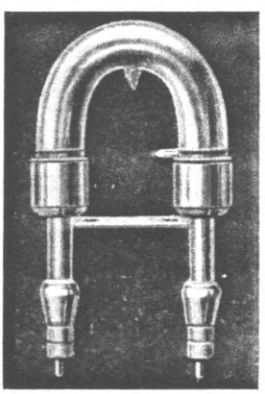


Fig. B 11-14B Combined W filament lamp and H.P. Hg lamp (cf. also Fig. B 20-67)

1 W filament; *2* Hg discharge tube, fused silica; *3* glass bulb; *4* internal phosphor coating; *5* outer reflecting coat; *6* support spring; *7* starter resistance; *8* lamp foot; *9* base

W filament is also series resistor for Hg discharge. Light sources: (*a*) filament, (*b*) Hg lamp, (*c*) phosphor (made by GEC and DUROTEST Co., type Fluomeric lamp. 25 lumens/W, life 12,000 hr)





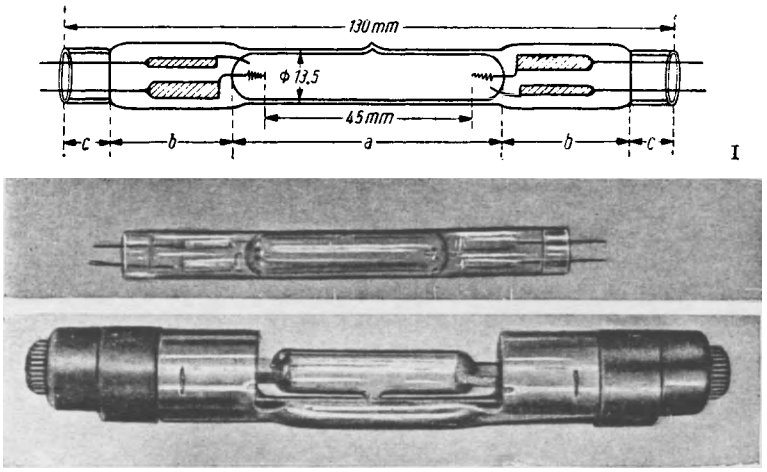
II

Fig. B 11-15 Low-pressure Hg lamp, U-shaped, with self-heating oxide cathodes and Ar striking-gas additive, for A.C. operation (made by QUARZLAMPEN-GES., Hanau)

I Design: *B* cathode diaphragm; *E* cathode; *D* current lead; *S* protective sleeve for thermal insulation of cathode space, to prevent Hg condensation and facilitate self-heating of cathode

II external view

so as not to jeopardize service personnel should a lamp fracture. Figure B 11-16 shows a lamp of this type with a globe bulb of about 5 mm wall fused silica, about 150 mm O.D. and capable of 25 kW input (= 40 W/cm² of inner bulb surface) (cf. Fig. B 20-68). When operating high-pressure Hg lamps, not only can too high a rating damage the bulb but too low a rating leads to overlong warm-up times, i.e. maximum light intensity takes too long to develop.



[11.9]

Fig. B 11-15A Low-pressure Hg lamp, straight type, with self-heating oxide cathodes Ar striking-gas and ignition electrodes (made by QUARZLAMPEN-GES., Hanau, type Q 600; voltage = 125, current = 1.7 A)

I design: *a* discharge tube section with cathodes and ignition electrodes; *b* flat pinch with two Mo foil seal-ins; *c* end sections
II photograph of exposed lamp source
III lamp, complete with reflector and holder

TABLE T 11-7. DIMENSIONAL DATA FOR HIGH-PRESSURE DISCHARGE LAMPS WITH FUSED SILICA ENVELOPES

I. From BOURNE (lamps similar to that in Fig. B 11-16)

POWER (W)	BULB DIAMETER		SPECIFIC SURFACE RATING	NOTES
	O. D.	I. D.	(W/cm²)	
250	30	24	10	Inside another sealed-off glass tube
500	40	34	14	
1000	45	39	20	Running in free air, cooled by convection
5000	85–90	80	25	
5000	65	53	47	Forced draught cooling
10,000	110	102	30	Convection cooling in free air

II. From THOURET

TYPE OF LAMP	OPERATING PRESSURE (atm)	BULB I.D. (mm)	ELECTRODE GAP (mm)	SPECIFIC SURFACE RATING (W/cm²)	NOTES
Tubular H.P.	3–15	6–16	> 15	10–15	Convection cooled
Globe, very H.P.	10–100	6–100	< 20	25–45	Convection cooled
	10–100	20–100	< 15	60–150	Forced cooling
Capillary, very H.P.	70–100	2	> 15	500–800	Water-cooled
For comparison: hard glass					
H.P. (max.)	0.3–3	20–60	> 40	3–4	Convection cooled

One type of Hg high-pressure lamp has recently come into use for film and TV studio lighting, and for research; these lamps have an arc length of only 12.5 mm, a start-up voltage of 10–15 V but a normal running voltage of 60–75. A similar construction is used for 1 kW Hg + Xe arc tubes with fused silica globes of only 50 mm dia., at the center of which a 6 mm arc forms between two W electrodes. Such lamps are used for

[11.9]

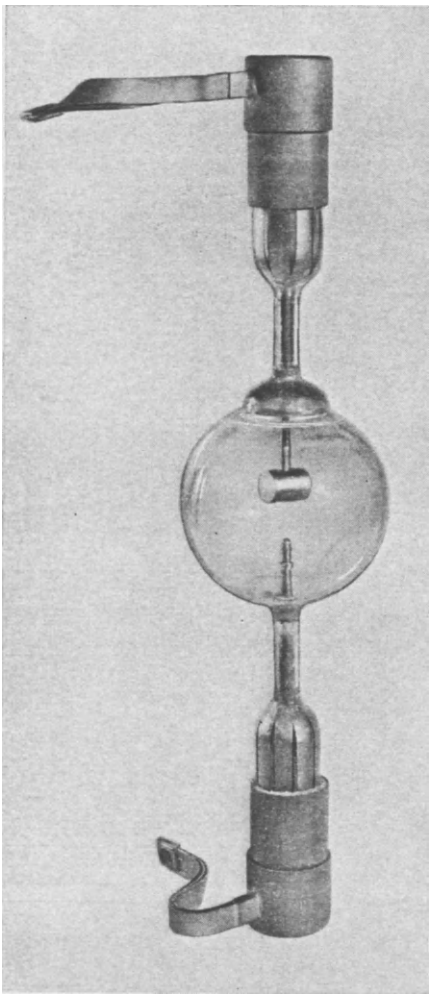


Fig. B 11-16 H.P. Hg lamp with fused silica envelope, 15 cm dia., 25 kW, for film studio lighting (made by GEC, Wembley, England) (FREEMAN, MANNERS)

marine signalling. See Chapter 20 (esp. Figs. B 20-25 and B 20-26) for H.P. lamps filled with several atmospheres of pure Xe, and with fused silica bulbs for color photography and projection.

The current lead-throughs in all the high-current lamps mentioned, which must carry up to 400 A or more in the largest constructions, are usually parallel-connected Mo strips sealed into the annulus between two concentric silica tubes. See Chapter 31 (Quartz-Metal Seals) for more details.

6. Tubular UV lamps for photochemistry, lengths from 17.5 cm (250 W) to 1.25 m (1400 W), the latter 12.5 mm O.D. Figure B 11-17 shows a photocopying lamp, Hg discharge type, with oxide cathodes and quartz disk diaphragms. In general, these lamps operate with only a few atmospheres Hg vapor. However, there are silica tube lamps with very high operating pressures on the market, such as 1000 W type H-6 of the GEN. ELEC. Co. with 80 mm tube length, 6 mm dia., and Hg pressures of 110 atm (WEITZ). [11.9]

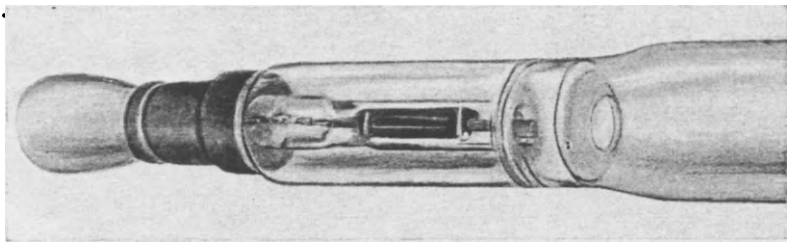


Fig. B 11-17 The end-section of a photocopying lamp (high-pressure Hg discharge) "HOK" type. Envelope of fused silica, with ring seal between it and the silica disk diaphragm; oxide cathodes and Mo foil seal-ins (ELENBAAS) (courtesy of PHILIPS)

The diaphragm has an opening of about 7 mm dia. and is placed 10 mm in front of the electrode; it serves the double purpose of centering the discharge and preventing blackening of large areas by condensates evaporated from the electrode

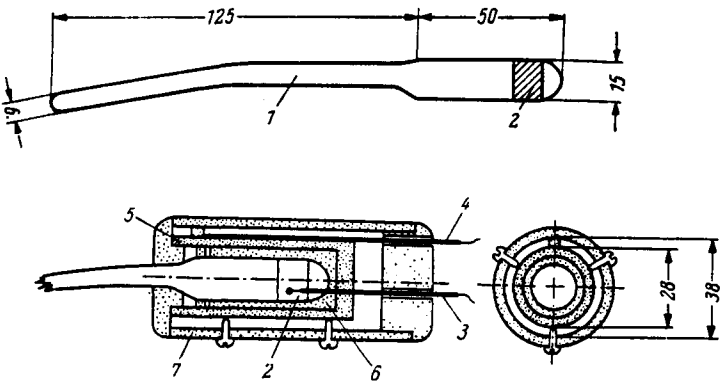


Fig. B 11-17A Electrodeless UV radiant lamp with fused silica envelope, for therapy, especially irradiation in body cavities; power input from H.F. oscillator (27 Mc/s) of a few watts output (ATKINS)

1 electrodeless silica tube filled with Ar or He (10 Torr) + Hg droplet; *2* outer electrode in the form of a Cu foil wrap, soldered to H.F. lead *3*; *4* second H.F. lead joined to a rod electrode parallel to 1, and 6 mm away from it; *5* internal support tube made of bakelite with rubber grommet *6*; *7* outer support tube, bakelite

7. Photographic flash-bulbs, 1 kW-sec per flash (see, e.g., ROBINSON).

8. The difficulty of metal-quartz sealing has led to the development of electrodeless UV lamps for certain medical purposes (ATKINS); these lamps are distinguished by long life, very low operating temperatures, low first cost and an external shape well suited to the application (Fig. B 11-17A).

(d) IR strip (soffit) lamps, made of quartzware with a central W filament coil. Rated at 40 W/cm coil length; this type of lamp with a glass bulb would only be rated at

3 W/cm. A typical commercial version for 500 W has a 200 mm length, I.D. 6 mm and O.D. 8 mm (WEITZ).

(e) Hg ejector and diffusion pumps of fused silica (Fig. B 11-18). These used to be preferred because of their thermal shock resistance (insensitivity to spray and condensing water) but nowadays they have largely been replaced by metal-body Hg pumps.

(f) Envelopes or windows for photocells with external photoelectric excitation (Fig. B 11-19). The figure shows one with fused silica window sealed to the envelope by a series of intermediate glasses.

[11.9]

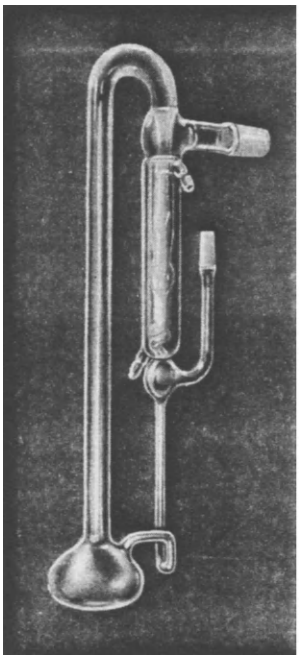


Fig. B 11-18 3-stage diffusion pump of fused silica (made by WESTDEUTSCHE QUARZSCHMELZE GmbH, Geesthacht/Elbe)

Speed at 10^{-3} Torr = 2 liters/sec, backing pressure needed = 15–20 Torr

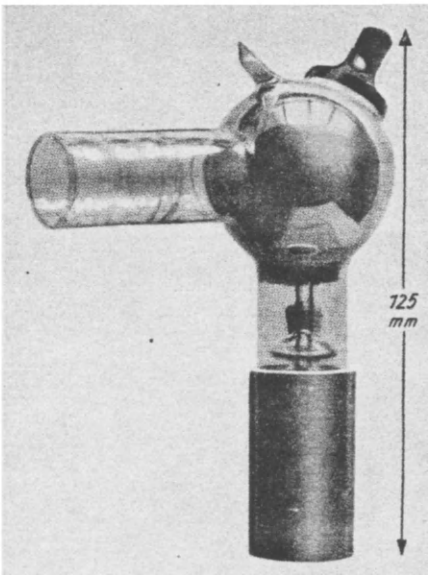
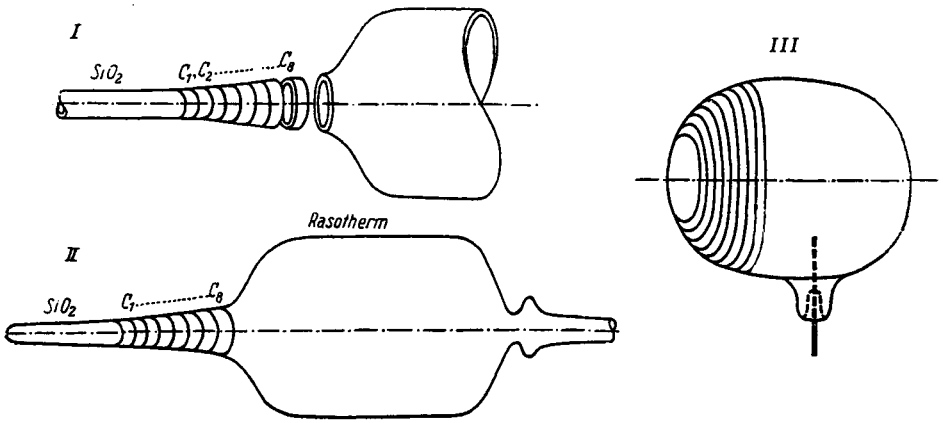


Fig. B 11-19 Photocell made of hard glass, with silica window (sealed via intermediate glasses) for measurements from IR to short UV (50,000–1500 Å)(courtesy of AEG (KLUGE)

There is a new process for sealing fused silica windows to hard-glass electron devices which results in a more appropriate shape of envelope than the classical process shown in Fig. B 11-19. GOERLICH has described the method: a conical tube is formed (Fig. B 11-19A, I) with a gradual increase in I.D.; this is done by joining a series of intermediate glasses, e.g. SCHOTT C 1 ($\alpha = 8 \times 10^{-7}$ 1/°C) to C 8 ($\alpha = 35 \times 10^{-7}$), of gradually increasing diameter. The wide end (C 8) is joined to a hard glass such as Rasotherm 4225^{III} ($\alpha = 31\text{–}33 \times 10^{-7}$, see Table T 10–4, D22) as

shown in position II of the figure. The cone of intermediate glasses has its narrow end (quartz) sealed off and the quartz blown out to a flat (position III).

(g) Hg switches with inserts of quartzware to protect the glass tube from the spark formed on break (cf. Fig. B 11-20).



[11.9]

Fig. B 11-19A Process for sealing fused silica window to hard-glass bulb

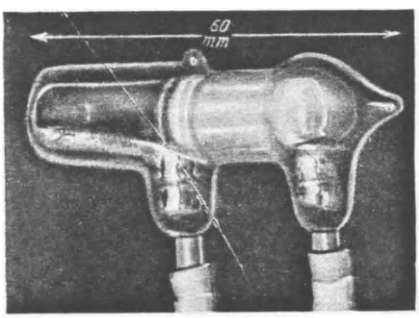


Fig. B 11-20 Hg switching tube with ground quartzware insert to protect glass wall from arcs

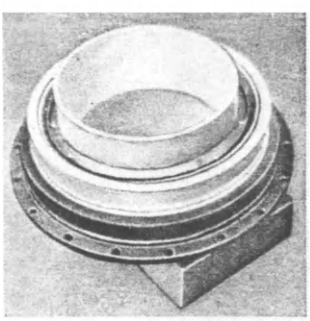


Fig. B 11-21 Quartzware insert ring used in construction of Hg cathode well of a 2000 A, 800 V tank rectifier (made by SIEMENS); cf. also Fig. B 5.3-4 B, No. 13

Outer insulator ring is porcelain, flange diameter about 750 mm, pool consists of about 60 kg Hg

(h) Piece-parts of Hg tank rectifiers, such as quartzware inserts to prevent formation of a cathode spot at the porcelain wall of the cathode pool well (Fig. B 11-21), or quartzware rings to prevent arc-back to the contact point between graphite plate

[11.9]

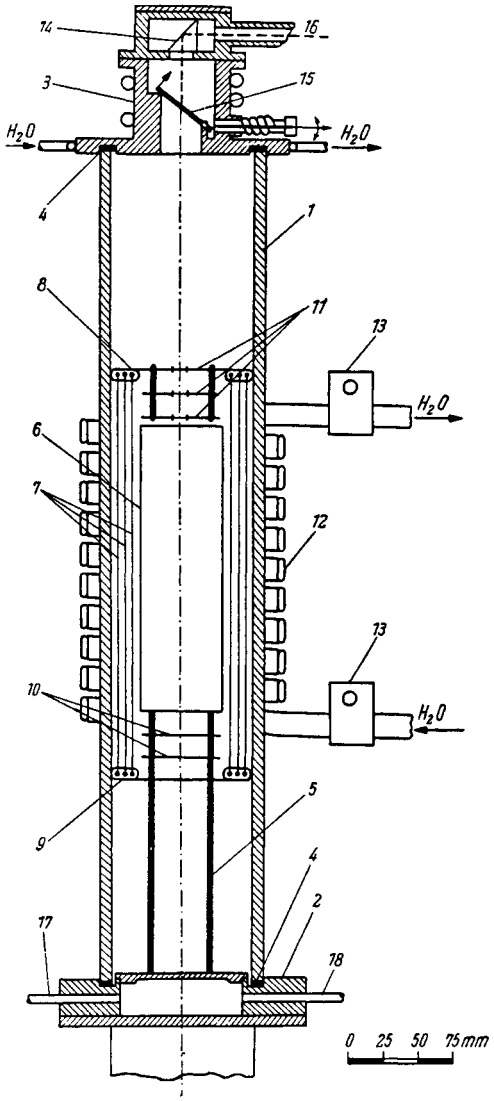


Fig. B 11-22 Induction furnace for 2300° max. internal temperature; fused quartz envelope *ca.* 110 O.D. and 570 mm long (P. D. JOHNSON)

1 silica tube; *2* pump flange; *3* water-cooled cover-plate; *4* rubber gasket; *5* support rods; *6* H.F.-heated crucible (200 mm long, 62.5 mm dia.) made of 1.25 mm Mo sheet; *7* radiation shield spiral, made of 0.25 mm Mo sheet; *8* insulator; *9* freely-suspended insulating weights; *10* lower heat shields; *11* upper heat shields with viewing holes; *12* H.F. work coil, water-cooled flattened Cu tubing; *13* H.F. leads; *14* total internal reflexion prism; *15* electromagnetically-operated screen for top observation window; *16* observation window for optical pyrometer; *17* air inlet; *18* to ion gauge

and porcelain lead-through insulator (Fig. B 8.5-15, 2) or deionization grids (Fig. B 8.5-15, 5). In general, direct and continuous contact between silica parts and the hot Hg arc should be avoided wherever possible, since silica will otherwise devitrify and embrittle after prolonged operation.

(i) Tubing for resistance-heated vacuum degassing furnaces (cf. Figs. B 9.2-11, B 9.2-15).

(k) Bell-jars for H.F. induction furnaces used for degassing, vacuum melting and sintering in vacuum or protective atmosphere (Figs. B 9.2-2c, B 9.2-13). Figure B 11-22 shows a carefully designed furnace for operating temperatures up to 2300°, using a quartz tube. [11.10]

(l) Capillaries for precision thermometers, since quartz shows no (secular) capillary depression effects as do ordinary silicate glasses (see 10.2.VII). A proven type of switch contact thermometer employs fused silica with a Ga filling and adjustable contacts to control furnace temperatures up to 1050° with the aid of a simple relay.

(m) Fused silica fingers, heated to 900° for introducing small amounts of He (see 11.5).

(n) Standard silica ground joints as per DIN 12248 (very small bore 3.7–51 mm), one-way taps as per DIN 12551, bores 1.5–15 mm; three-way taps (DIN 12554), 2.5–6 mm bore; ball-joints (ball + socket) with ball diameter 12–55 mm and tube I.D. 6–40 mm. (Made by WESTDEUTSCHE QUARZSCHMELZE GmbH, Geesthacht/Elbe.)

(o) Quartz protection tubes for Pt-PtRh thermels, see 4.1 (chemical properties of Pt, Vol. 1).

11.10. Technical Applications of Vycor Glass

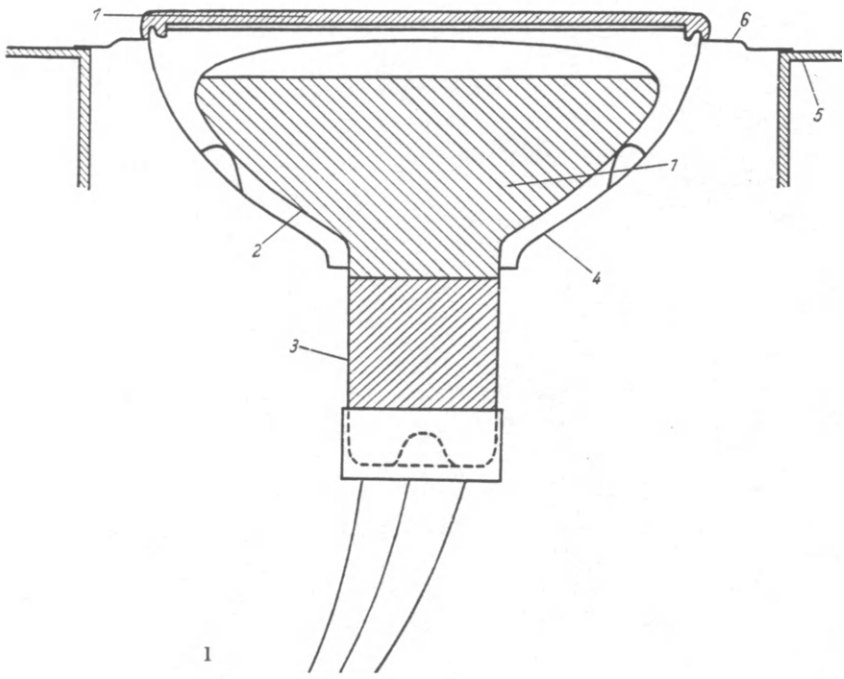
CORNING 7900–7911 are available in the same forms as ordinary technical silicate glasses (Table T 10–4, A 1). Many possibilities for application have been tried out to date. The following have been put into practical use:

(a) UV therapy lamps with low-pressure Hg discharge for medium- and long-wave UV (Fig. B 11-8) without troublesome ozone formation, especially the so-called "germicidal lamps" (SHAVER). (UV of 1300–2000 Å forms O_3, UV around 2537 Å is bactericidal and excites certain phosphors to luminescence, while the long waves around 3000 A can be used for therapeutic purposes (cf. Fig. B 11-8A).)

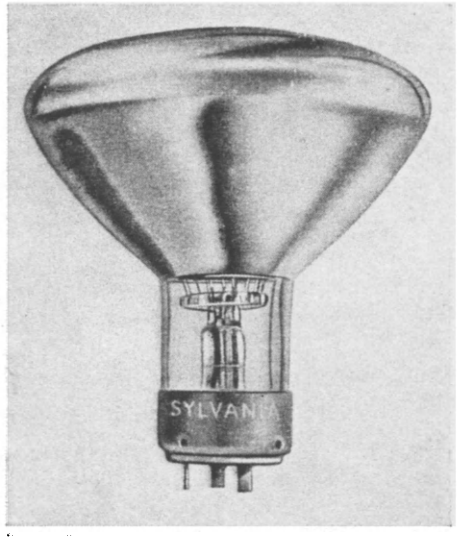
(b) IR radiant lamps for domestic cooking ovens: Fig. B 11-23 shows the arrangement. For 1250 W dissipation, the bulb is Vycor and the size is the same as an ordinary 150 W bulb of hard silicate glass. It is coated internally with a gold reflector layer and provided with an intermediate glass neck to allow sealing to W current leads. Although the bulb surface temperature is 600° it can be sprayed with ice-water without cracking.

(c) High-power W filament lamps (e.g. 1 kW) with a dead weight below $^1/_2$ kg for outdoor operation without rain-guards (SLAUER).

[11.10]



I



II

Fig. B 11-23 **IR radiant lamp with 1550 W tungsten filament system in Vycor glass bulb for domestic cookers (SLAUER)**

I design: *1* Vycor bulb; *2* evaporated reflector layer of Au; *3* bulb neck of intermediate glasses with exhaust stem and W leads; *4* bulb-holder and exterior reflector; *5* cooker top-plate; *6* sealing ring; *7* red-tinted protective plate of Vycor glass

II photograph of lamp

III

Fig. B 11–23 IR radiant lamp with 1550 W tungsten filament system in Vycor glass bulb for domestic cookers (SLAUER)
III view of arrangement in cooker

[11.11]

11.11. Other Applications of SiO_2

SiO_2 can be produced in thin layers and as a binder from ethyl silicate in reaction with H_2O:

$$(C_2H_5O)_4Si + 3H_2O = H_2SiO_3 + 4C_2H_5OH$$

(see also 9.4.XIII). When heated, the alcohol evaporates, the silicic acid dehydrates and produces a fine, highly-reactive form of SiO_2. Since the original form of ethyl silicate is unstable and gels after a time in the presence of water vapor in the air, a series of modified silicone esters have been developed that will deposit SiO_2 but are more stable because of retardation agents and therefore have longer storage life (see COGAN). They are commercially available under the name "Silesters" (SILICON DEVELOPMENTS LTD.). In another process, H_2SiO_3 is suspended in acetone and applied to metal surfaces. When the acetone is dry, the coating is heated to drive off bonded water, and again a SiO_2 layer is left (see, e.g., GOULD).

See 10.4.V (Protective Coatings) for quartz-coating metalized objects by cracking ethyl silicate vapor in vacuum at temperatures up to 850°.

See 10.4.V for evaporation of SiO_2 on optically-worked glass or evaporated metal coatings to protect against weathering.

Chapter 31 gives a comprehensive treatment of quartz-metal seals and other vacuum-tight current leads in quartz glass envelopes.

11. 12. References

ALEXANDER-KATZ, B.: *Quarzglas und Quarzgut* (Braunschweig, 1919)

ANGERER, E. von: H. EBERT editor: *Technische Kunstgriffe bei physikalischen Untersuchungen*, 9th ed. (Braunschweig, 1954) (p. 116, Manufacture of quartz fibers)

ANON.: *Illumin. Engng.* **49** (1954) 361 (Hg lamps with internal silica element)

ASKENASY, X.: in M. PIRANI: *Elektrothermie* (Berlin, 1930), p. 140

ATKINS, C. E.: *Rad. and Television News* (March 1951), pp. 36–37, 134 (Electrodeless UV radiant lamps for medical purposes)

BARRER, R. M.: *Diffusion in and through Solids* (Cambridge, 1951)

[11.12]

BAUKLOH, W., and A. HOFFMANN: *Ber. dtsch. keram. Ges.* **15** (1934) 424 (H_2 permeability of fused silica)

BERAN, C. M.: *Sklář a keramik* **6** (1956) 261–263 (Manufacture and properties of Vycor glass)

BERLINER QUARZSCHMELZE: *Special Prospectus VLK 3507* (Berlin, 1935) (Chemical behavior of fused silica)

[1]BOTTOMLEY, I.F., and A. PAGET: DRP 170 234 (Manufacture of quartzware tubes in rotary kiln)

[2]BOTTOMLEY, I. F., and A. PAGET: DRP 174 509 (Forming tongs for blowing silica with compressed air)

BOURNE, H. K.: *Discharge Lamps for Photography and Projection* (London, 1948)

BRIGGS, L. J.: *J. Phys. Chem.* **9** (1905) 617 (Thickness of water film on fused silica)

COGAN, H. D., and C. A. SETTERSTROM: *Ind. Eng. Chem.* **39** (11) (1947) 1364–1368 (Deposition of SiO_2 from liquid solutions)

COHEN, J.: *J. Appl. Phys.* **28** (1957) 795 (Electrical resistance of fused silica at very high temperatures)

[1]CORNING GLASS WORKS: Bulletin B–83: *Properties of Selected Commercial Glasses* (Corning, N. Y. 1949)

[2]CORNING GLASS WORKS: Bulletin B–91: *Vycor Brand Industrial Glassware by Corning* (Corning, N. Y. 1956)

D'ANS, J., and E. LAX: *Taschenbuch für Chemiker und Physiker*, 2nd ed. (Berlin, 1949)

DOUGLAS, R. W., and J. O. ISARD: *J. Sci. Instr.* **29** (1952) 13–15 (Thermal expansion of fused silica)

EBERT, H.: *Die Wärmeausdehnung fester u. flüssiger Stoffe* (Braunschweig, 1943) (α)

ELENBAAS, W., and K. R. LABBERTÉ: *Philips Techn. Rdsch.* **13** (1952) 305–309 (High-pressure Hg discharge lamps of fused silica for photocopy work)

FISCHER: *Die Technik, Messesonderheft* (1955) p. 133 (Silibor glass)

FORTEY, J.: *Fused Quartz Manufacture in Germany*, BIOS Final Report No. 1202, pp. 1–6 (London, 1947)

FREEMAN, G. A.: *Westinghouse Engineer* (March 1950), pp. 105–106 (Very high pressure Hg discharge lamps with silica glass bulbs)

FRITZ-SCHMIDT, M., GEHLHOFF, G., and M. THOMAS: *Z. Techn. Phys.* **11** (1930) 325 (IR transmission of fused silica)

GABOR, D.: DRP 573448/31/33 (Metal foil-to-quartz seals made by arc heating)

GIALANELLA, J.: *Chem. Eng.* **60** (1953) 302 (Fused silica)

GOERLICH, P., and A. KROHS: *Vakuumtechnik* **5** (1956) 12–17 (Sealing quartz windows to hard glass tubes)

GOULD, H. L. B.: *Bell Lab. Rec.* **28** (1950) 292 (Insulation of metal surfaces with SiO_2 deposited by cataphoresis)

GROSS, M. I.: *Fused Quartz Manufacture in Germany*, FIAT Report No. 536 (London, 1945)

GÜNTHER, P.: *Quarzglas* (Berlin, 1911)

GUYER, E. M.: *Proc. IRE* **32** (1944) 743–750 (Electrical surface resistance of fused silica)

HÄNLEIN, W.: *Glastechn. Ber.* **18** (1940) 308–314; see also US Pat. 2 115 131 (Tube-drawing machine for fused silica, with Mo crucible and Mo draw-die)

HIPPEL, A. R.: *Dielectric Materials and Applications* (London, 1954)

HOOD, H. P., and M.E.NORDBERG: US Pat. 2 106 744/34/38; cf. also US Pat. 2 215 039/34/40, 2 221 709/38/40, 2 286 275/40/42 (Manufacture of sintered quartz glass "Vycor", with more than 95% SiO_2)

JOHNSON, J., and R. BURT: *J. Opt. Soc. Amer.* **6** (1922) 734 (Ar permeability of fused silica)

JOHNSON, P. D.: *J. Amer. Ceram. Soc.* **32** (1949) 316–319 (H.F.-induction furnace for use up to 2300° with fused silica tube)

JOSSEN, E. L.: *Rev. Sci. Instr.* **11** (1940) 164 (Heated silica glass tube as membrane for introducing gas)

KERN, J.: *ETZ* (B) **6** (1954) 67–72 (Production of UV for medical purposes)

KINGERY, W. D.: *J. Amer. Ceram. Soc.* **38** (1955) 252 (Thermal conductivity of fused silica as a function of temperature)

KITAJGORODSKIJ, J. J.: *Doklady Akad. Nauk SSSR* **64** (1949) 219; *idem: Sklo a tavení skla* (Prague, 1952)

KLUGE, W.: *Z. Techn. Phys.* **16** (1935) 184 (Alkali photocells)

KOELLER, L. R.: *Ultraviolet Radiation* (New York, 1952)

KREIDL, N.: *Sklářské rozhledy* **22** (1946) 85 (Vycor glass)

KUTSCHENREITER, M.: *Silikattechnik* **5** (1954) 439–440 (Manufacture of quartzware in carbon rod electric furnace, from rock crystal grit)

LADOO, R. B.: *Mining and Metallurgy* **28** (1947) 501–503 (Production of clear fused silica)

LILLIE, H. R.: *44th Annual Meeting of Amer. Ceram. Soc.* (April 1942), quoted by M. E. NORDBERG (q.v.) [11.12] (Expansion characteristic of fused silica)

MANNERS, M.: *Elect. Eng.* **25** (1953) 512–513 (Use of fused silica for transmitter tubes and high-pressure Hg lamps)

MOHN, H.: *Glastechn. Ber.* **29** (1956) 483–487 (Recent silica glasses made by HERAEUS, Hanau, absorbing in the short-wave UV range; type E for low-pressure lamps, type 38 and sheath glass type 38 for H.P. lamps with internal silica elements; these glasses prevent formation of O_3)

[1]NORDBERG, M. E.: *J. Amer. Ceram. Soc.* **27** (1944) 299–305 (Properties of Vycor glass)

[2]NORDBERG, M. E.: US Pat. 2 505 001/1946/1950 (Manufacture of Vycor (>95% SiO_2) of specially high UV transmission)

NORTON, F. J.: *J. Amer. Ceram. Soc.* **36** (1953) 90–96 (Diffusion of gases, esp. He, through technical glasses); see also *J. Appl. Phys.* **28** (1957) 34–39

OUWELTJES, J. L. *et al.: Philips Techn. Rdsch.* **13** (1951) 113–123 (H.P. Hg lamps made of small silica tubes with 2nd glass (outer) envelope)

OWEN, A. E., and R. W. DOUGLAS: *J. Soc. Glass Techn.* **43** (1959) 159 T–178T (Electrical properties of fused silica of different purities)

PARKS, G. J.: *Phil. Mag.* **5** (1903) 617 (Thickness of water films on fused silica)

PHILIPS, C. J.: *Glass, the Miracle Maker*, 4th ed. (New York, 1948)

REIMANN, A.: *Vacuum Technique* (London, 1952)

REINKOBER, O.: *Phys. Z.* **32** (1931) 243; **38** (1937) 112 (Tear strength of fused silica fibers)

ROBINSON, N. W.: *Philips Techn. Rdsch.* **16** (1954) 173 (Electronic flash-bulbs of quartz glass)

RUFF, O., and Z. SCHMIDT: *Z. anorg. allgem. Chemie* **117** (1921) 172 (VP of SiO_2 and SiO)

RUSSELL, A. S., and J. J. STOKES: *J. Amer. Chem. Soc.* **69** (1947) 1316 (Diffusion of H_2 through Vycor glass)

S.A. DES MAN. DES GLACES, St. Gobain: Swiss Pat. 167752 (Melting and drawing machine for silica glass tubing)

SAUNDERS, J. B.: *J. Res. Nat. Bur. Stds* **28** (1942) 51 (Thermal expansion of quartz glass and sintered Vycor glass)

SCHÄFER, H., and R. HÖRNLE: *Z. anorg. allgem. Chemie* **263** (1950) 261 (VP of SiO)

SCHURKOW, S.: *Phys. Z. der Sowjetunion* **1** (1932) 123–131 (Tear strength of quartz fibers)

SCHWERTZ, F. A.: *J. Amer. Ceram. Soc.* **32** (1949) 390 (Porous Vycor glass)

SEEMANN, H. E.: *Phys. Rev.* **29** (1927) 616; **31** (1928) 119–129 (Thermal conductivity and resistivity of fused quartz)

SHAVER, W. W.: *Illumin. Engng.* **45** (1950) 543 (Use of Vycor for illumination purposes)

SILICA SYNDICATE: DRP 241260/1910/11 (Clear fused silica)

SINGER, F.: "Geschmolzener Quarz" in M. PIRANI: *Elektrothermie* (Berlin, 1930)

SLAUER, R. G.: *Illumin. Engng.* **45** (1950) 544 (Vycor glass for high-power W filament lamps, e.g. IR cookers)

SMEKAL, A.: *Glastechn. Ber.* **23** (1950) 360 (Manufacture of sintered quartz glass "Vycor")

SOSMAN, R. S.: *Properties of Silica* (New York, 1927)

SOUDER, W., and P. HIDNERT: *J. Res. Nat. Bur. Stds.* **21** (1926) (1α of quartz)

STRAUSS, S. W. *et al.: J. Res. Nat. Bur. Stds.* **56** (1956) no. 3, p. 135 (Electrical resistance of fused silica)

STRONG, J.: *Modern Physical Laboratory Practice* (London, 1944) (p. 188: Use of fused silica)

TAYLOR, H. E.: *J. Soc. Glass Techn.* **39** (1955) 193 T (Electrical resistance of fused silica)

THOMPSON, T. J.: *Ceram. Bull.* **31** (1952) 290–291 (Porous glass Vycor 7930)

THOMSON, E.: US Pat. 778 286/1902/1904 (Melting quartzware tubing from sand with an electrically heated carbon core)

THOURET, W.: *Lichttechnik* **2** (1950) 73–79, 107–110 (Quartz discharge lamps)

TSAI, L. S., and L. HOGNESS: *J. Phys. Chem.* **37** (1932) 2595 (Diffusion of gases through fused silica)

VOLAROVICH, M. P., and A. A. LEONTIEVA: *J. Soc. Glass Techn.* **20** (1936) 136–143 (Viscosity of molten silica glass)

VOLF, M. B.: *Technická skla* (*Technical Glasses*) (Prague, 1953)

[11.12] WATSON, H. L.: *J. Amer. Ceram. Soc.* **9** (1926) 511–534 (Properties of quartz and quartz glass)

WEITZ, C. E.: *Illumin. Engng.* (Nov. 1954) 513–519 (Manufacture and use of fused silica)

CHAPTER 12

CERAMIC MATERIALS OF HIGH VACUUM TECHNOLOGY

(1,2ALBERS-SCHÖNBERG, BUDNIKOW, DEMUTH, GALLET, HECHT, LIEBSCHER, SCHÄTZER, SOMMERFELD; see also 2KINGERY) [12.1]

THE scope of this book and especially of this chapter restricts the discussion to ceramic materials used in vacuum work or those that might be used there: therefore the main group treated is that of *capacitor* ceramics, of great importance in other technologies. In what folllows, "ceramic materials" is shortened to "ceramics" in accordance with recent usage as with "glass", "mica", "metals", etc., although the term "ceramics" at one time referred only to the general *technique* of manufacture.

There are three basic types of ceramics: silicates, pure oxides, and special ceramics such as those which contain carbides. The last type has not so far become important in vacuum technique.

12.1. Silicate Ceramics

These are mixtures of inorganic crystalline substances (almost always metal oxides) with glassy, silicate-type fluxes and binders in widely different amounts, which form (at room temperature) a plastic, fictile starting material. When molded, this mass only attains the final shape and properties (especially strength) during firing.

12.1.I. *Raw materials*

The main point to notice is that, for reasons of economy and technique, these materials are not made synthetically with the desired purity. They are usually naturally occurring minerals with more or less variable composition (impurities) and different properties; even when the chemical composition is the same, the rheological properties of clay from various sources often vary. This produces ceramics whose properties vary a good deal, although many impurites like pyrites in clay or quartz sand in raw kaolin are removed by preparatory processes.

The chief minerals and their main chemical properties of concern to manufacture of silicate ceramics are given in Table T 12–1, which also contains a series of silicate compounds which are often formed in varying amounts from the start-out mass only by firing.

When selecting mineral raws and preparing the plastic batch, efforts may be made to eliminate, where possible, sources of uncertainty due to the origin of the mineral. The vacuum technologist usually requires high quality from materials but in many cases he cannot demand the reproducibility of composition and behavior from ceramics that

TABLE T 12-1. COMPOSITION OF CRYSTALLINE STARTING MATERIALS AND CONSTITUENTS OF CERAMICS

DESCRIPTION OF MATERIAL	COMPOSITION (w/o)
Ball clay (English)	See clay
China clay (English)	See kaolin
Cordierite	$2\,MgO \cdot 2\,Al_2O_3 \cdot 5\,SiO_2$ (14/35/51%)
Cristobalite	SiO_2, high temp. form
Enstatite	$MgO \cdot SiO_2$ (40/60)
[12.1] Feldspars (minerals)	
potash feldspar (orthoclase)	$K_2O \cdot Al_2O_3 \cdot 6\,SiO_2$
soda feldspar (pericline)	$Na_2O \cdot Al_2O_3 \cdot 6\,SiO_2$
lime feldspar (anorthite)	$CaO \cdot Al_2O_3 \cdot 2\,SiO_2$
Flint (mineral)	SiO_2
Forsterite (magnesium orthosilicate)	$2\,MgO \cdot SiO_2$ (57/43)
Calspar (mineral)	$CaCO_3$
Kaolins (raw)[1]	Rock with up to 40% kaolinite (q.v.)
Kaolinite[1]	$Al_2O_3 \cdot 2\,SiO_2 \cdot 2\,H_2O$
Quartz	SiO_2
Clinoenstatite	$MgO \cdot SiO_2$ (40/60)
Corundum (alumina)	Al_2O_3
Magnesite (mineral)	$MgCO_3$
Mullite	$3\,Al_2O_3 \cdot 2\,SiO_2$ (72/28)
Periclase	MgO
Pyrophyllite (mineral)	$Al_2O_3 \cdot (3\text{–}4)\,SiO_2 \cdot H_2O$
Rutile (mineral)	TiO_2
Grog	Crushed or ground (burned) fireclay[4]
Barytes (mineral)	$BaSO_4$
Sillimanite (mineral)[2]	$Al_2O_3 \cdot SiO_2$ (63/37)
Soapstone (mineral) = steatite or talc	Pure: $3\,MgO \cdot 4\,SiO_2 \cdot H_2O$ (31.8/63.4/4.8); the solid cryptocrystalline rock is mostly: $(3\text{–}4)MgO \cdot (4\text{–}5)SiO_2 \cdot (1\text{–}2)H_2O$ (+ 5–15% impurities)
Steatite (mineral)[3]	See soapstone
Spinel	$MgO \cdot Al_2O_3$ (28/72)
Talc	As soapstone, but the flake or foliated form
Talcum (= French chalk)	Fine-ground white talc
Clay (mineral)	Plastic, hydrated Al-silicate $Al_2O_3 \cdot (0.3\text{–}0.8)\,SiO_2 \cdot (0.5\text{–}19)\,H_2O$ (chief group: kaolin (q.v.)) + quartz + lime + hydrated iron oxide
Tridymite	Allotrope of quartz (q.v.)
Zircon (mineral)	$ZrO_2 \cdot SiO_2$

(1) In practice, "kaolin" generally means suspensions of kaolin, consisting almost entirely of pure kaolinite. This material is also known as "porcelain clay" because of its color after firing which results in its use mainly in manufacture of porcelain.

(2) Sillimanite *mineral*. Not to be confused with synthetic material sold under the same name or with commercial fine-grain ceramic of DIN Type 610 (Table T 12-11, D α).

(3) Steatite *mineral*. Not to be confused with commercial ceramic of the same name.

(4) Shamotte or fireclay is a coarse ceramic made by firing a low-flux clay with addition of pre-fired material.

he would get from most of his other materials, even technical glasses when drawn from different manufacturers. Besides, preparation of the initial sludge and the temperature-time schedule of firing can exert a crucial influence on composition, structure and properties, so that mere chemical analysis, apart from the questions of difficulty and time-consumption, offers no possibility of adequate quality control of feed materials for ceramic components.

The composition of various types of ceramics is treated in detail in 12.3 below. By and large, all silicate ceramics are made from plasticizing (fictile) minerals with additions of non-fictile inorganic substances, again (usually) naturally occurring minerals. The [12.1] main plasticizing minerals must be pretreated to some extent; clay, especially the kaolins, in natural form, talc and soapstone (steatite) are the chief ones. Steatite must first be thoroughly ground. Every clay is a mixture of minerals and the mix ratios are widely divergent. Each deposit supplies typical but often very different kinds of clay. Evenly-moistened clay, as air-free as possible, gives the sludge the plasticity needed for forming. The fictility of clay originates in formation of water at the surface of the crystals of kaolinite, a characteristic constituent of all clays; this enables the crystals to cohere and slide across each other. The plasticizing effect of ground magnesium hydrosilicate (talc and soapstone) is apparently caused by adsorption of the make-up or tempering water at the surfaces of the fine particles. Make-up water means the amount of water needed to give clay, kaolin or mix of these with other materials a fictile mass which just does not stick to the hands (ENDELL). In addition, clay has a high content of glass formers (alkali, BaO, CaO, FeO, etc.) which produce a glassy phase in the firing process; in porcelains, this phase amounts to 50–70%. Since many new ceramics are required to have high strength and improved insulation properties for electrical work, there has been a tendency to reduce this glassy phase and hence the clay content as far as possible. One way is to increase the content of ground talc or soapstone; in extreme cases, the necessary fictility must be achieved by suitable milling processes for the components and by use of organic binders and plasticizers like nitrocellulose, traganth, etc. Obviously, these materials are completely removed during the subsequent air-furnace firing before the actual sintering process. A certain degree of plasticity can be achieved without plasticizers by adding acid to the make-up to etch the surfaces of the particles and so make them reactive with water. The particles thus become covered with a water skin or hydroxide layer which, as with clay addition, facilitates coherence and mutual slip of the individual grains, to which the plasticity of the ceramic mass is proportional (see also 12.6).

The manufacture of such low-clay or clay-free ceramics, a group to which the pure oxide ceramics obviously belong (see 12.6), is generally far more difficult than that of the orthodox porcelains with high clay content, and in technology is therefore limited to cases where the latter type are inadequate.

Besides the plasticizers, the ceramic sludge will also have a series of additives which depends on the properties to be obtained in the final product in firing. These "lean" materials are non-plasticizing, and are either derived from minerals such as quartz sand, flint, feldspar, barytes, magnesite, sillimanite, mullite and recently zircon, or are manufactured, such as Al_2O_3, MgO, ZrO_2 and also TiO_2 (rutile) for capacitor materials not treated here.

Choice of composition of a ceramic mass is not, however, solely determined by the required mechanical and electrical properties of the end product. In practice, it is often fixed by the magnitude of the sintering range which depends on composition. This term means the difference in temperature between onset of sintering ("vitrification") and the

[12.1]

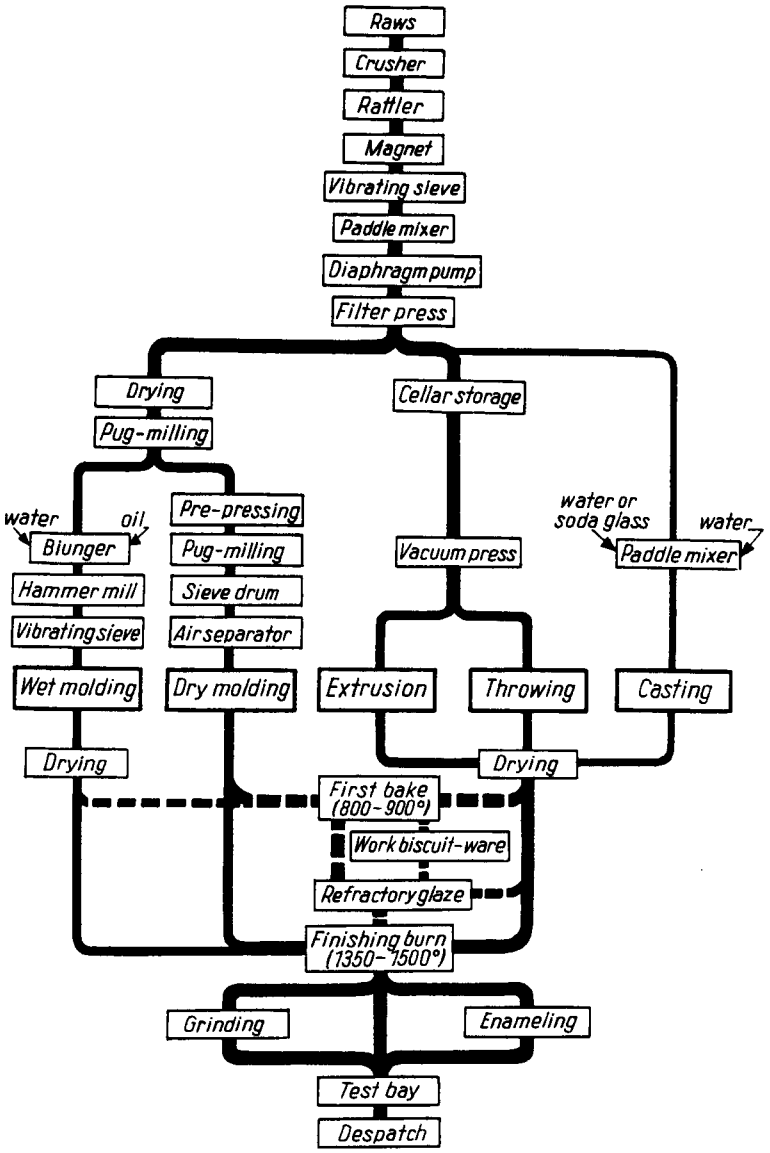


Fig. B 12-1 Scheme of the manufacturing process of ceramic insulating materials for high-frequency techniques (by HESCHO)

onset of deformation of the piece, in the process of firing. Clearly, the rate of rejection and the capital outlay on mass-production in a kiln running at 1370° is different for sintering intervals of 30°, or only 10°.

12.1.II. *Raw Materials Handling*

Although handling of raw materials for sludges and fired ceramics differs at many points for individual types of ceramic, a fairly universal schedule can be drawn up for the basic process, as shown in Fig. B 12-1, and which runs as follows:

[12.1]

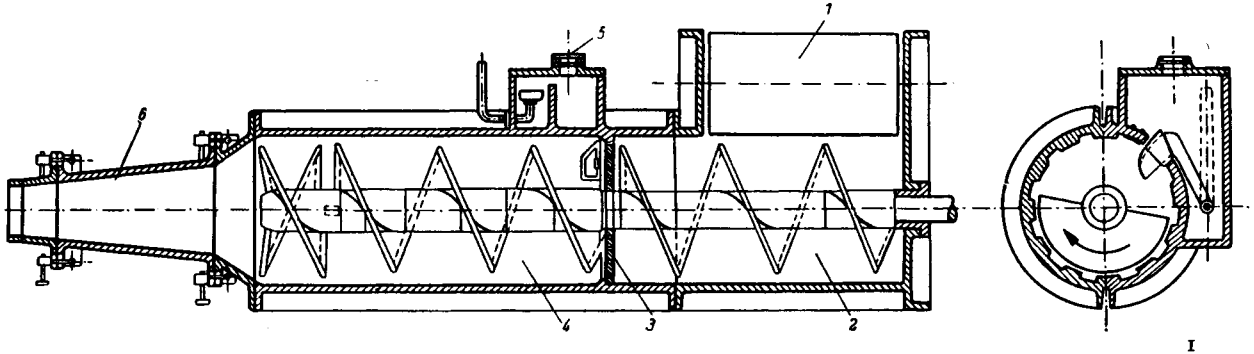
Usually, the mineral constituents of a ceramic batch are first comminuted in crushing rolls, rock crushers and pug-mills. They are then fine ground by wet ball-milling, possibly also elutriated in water to size the grains; this applies particularly to clays and kaolin. The resulting sludge is fed past an electromagnet to remove Fe particles and then pumped through a filter press which expels excess water by application of 6–8 atm pressure to force the sludge through a cloth filter. The filter cake which remains between the cloths is a few centimeters thick; it is dried to the point where it can be powdered and granulated. Where no plasticizer mineral (clay, etc.) is already present in the mass, organic binder (see above) and make-up water is added, and after blunging, the plastic paste which results is often deaerated in a vacuum press (Figs. B 12-2 and B 12-2A) at 30–50 Torr. These or similar methods are used to produce a mass of material homogeneous in air content, moisture and structure which only then can be made into ceramic bodies, by plastic working (extrusion, throwing, hand-modeling).

12.1.III. *Forming the Ceramic Starting Mass*

The following methods are the main ones for forming the mass before firing; the water content has to be appropriate to the method:

1. *Forming by throwing (spinning) or extruding the mass in the moist, plastic state.* The water content lies between 20% and 30% according to the type of mass. Throwing is done on a potter's wheel or jigger on which the plastic lump is modeled, as in pottery work, by hand or strickle and plaster of Paris mold to make radially symmetrical pieces. In extrusion pressing of rods, a solid cylindrical plastic lump is first deaerated by evacuation, then rammed through a die (Fig. B 12-3). In the same way tubes can be made, but a core is inserted in the die mouth, corresponding to the I.D. of the tube (Fig. B 12-3A). Figure B 12-3B shows two horizontal vacuum extrusion presses, small compared to that in Fig. B 12-2; here the starting lump is deaerated and extruded to small rods or tubes in one pass.

2. *Slip casting.* The starting mass is blunged with about 15–40% make-up water plus small amounts of basic electrolytes such as soda (Na_2CO_3), water-glass (Na_2SiO_3), potash (K_2CO_3), or NaOH. The suspension, sludge or slip should not settle out even after standing. For vacuum-tight hollow-ware it is recommended that the slip is well deaerated before casting by prolonged stirring under reduced pressure (see, e.g., HURSH). For hollow casting work, one uses a demountable, well-dried, porous plaster of Paris mold (Fig. B 12-4, A). The suction power of the plaster extracts water from the regions of the slip near the wall, and after a certain standing time a solid sheath of desired thickness forms on the inner wall of the mold. The unset slip is decanted and the mold



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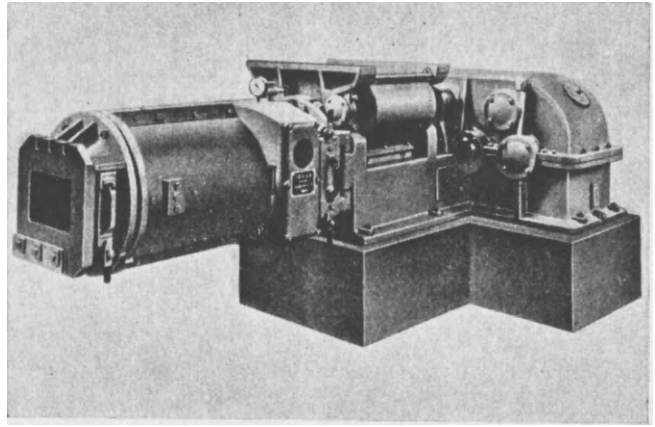


II

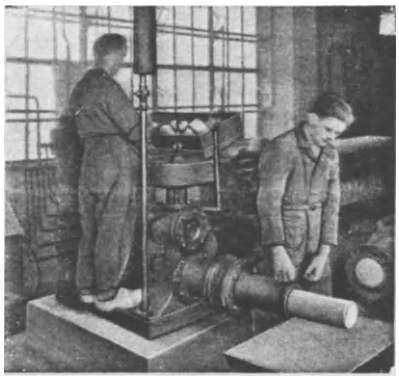
Fig. B 12-2 Example of vacuum press for deaerating ceramic batch (made by C. KELLER UND CO., Langenbeck, Westph., Germany) (see also HEIL)

I schematic cross-section: *1* entry port for the filter-cake; *2* pre-pressing space for homogenization of cake by mixing and kneading; *3* narrow slit for separating the cake into fine strands for intensive deaeration; *4* vacuum chamber; *5* connexion for vacuum pump (e.g. water ring pump with 20 Torr ultimate); *6* press heat for attachment of various shapes of nozzle.

II overall view of press

and shard dried. The shard shrinks after a while and can easily be removed from the mold and dried further.

Hollow casting is the preferred method for making thin, even-walled vessels (2–8mm wall), and core casting is used for making shards of variable thickness (Fig. B 12-4, B).



[12.1]

Fig. B 12-2A A vacuum press in action (courtesy of PHILIPS, Eindhoven) (IJDENS)

3. *Wet molding of semi-dry (friable) state.* The lump is mixed with water and lubricant oil; the amount of free water varies from 12% to 20% according to composition of the lump. The mix is heaped on the pinch-off mold of the press (Fig. B 12-5) to provide excess material.

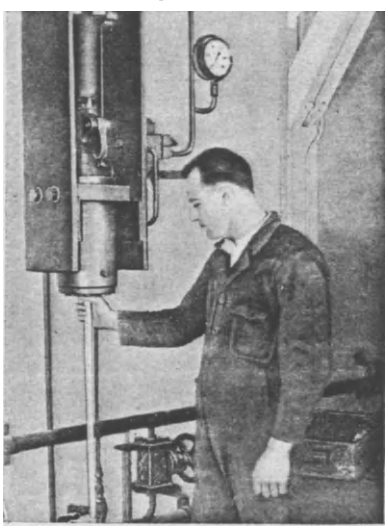


Fig. B 12-3 Manufacture of rod or tube from a ceramic batch with a vertical-ram extrusion press (IJDENS)

In the upper press cylinder there is a pre-pumped cylindrical batch which is forced through a die of suitable shape; another version of this type of press can be seen in the background of Fig. B 12-3B

4. *Dry pressing* of finely powdered and precise doses of starting material, water content 6–12% (Fig. B 12-6). In this process the pressure applied is far higher than that in wet molding. The method is used specially for mass-production of small insulator tubes and components that must have tight tolerances without the need for finishing

grinding. (See, e.g., STANISLAW.) Figure B 12-6A shows a semi-automatic machine for this purpose.

In general, ceramic parts made by method (3) have lower mechanical and electrical strength and higher porosity than those made by (1), (2) and (4).

[12.1]

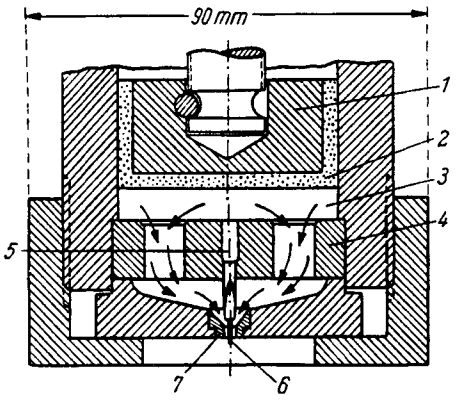


Fig. B 12-3A Section through a device for molding thin ceramic sleeves (e.g. for I.H. cathodes ([1]NAVIAS)

1 press die; *2* leather washer; *3* plastic mass; *4* disk with seven holes each 10 mm dia.; *5* plug-holder; *6* plug, where tube I.D. is small, made of W wire; number, diameter and arrangement set by desired bores; *7* nozzle, made of cemented carbide, e.g. W_4C

12.1.IV. *Drying and Firing*

The pressings are first dried in air, possibly in special, heated chambers (Fig. B 12-7). They are still very brittle, but with a few precautions can be worked by machine tools which do not lift a chip but "grind" the material. The pressings are then more or less

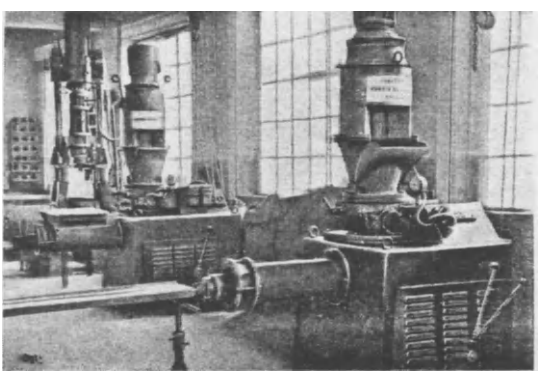
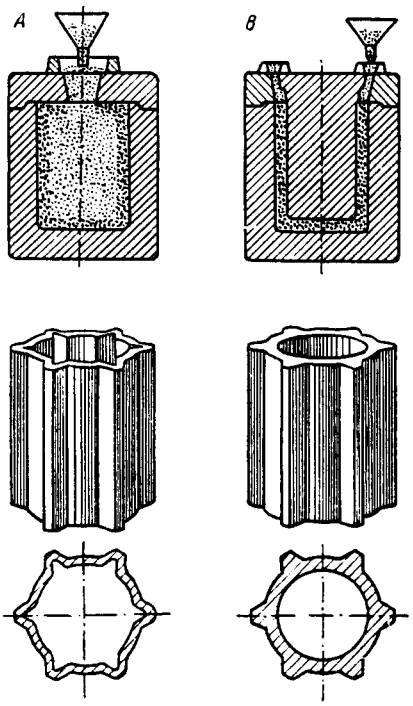


Fig. B 12-3B Small horizontal vacuum extrusion presses, with vertical loading chambers, for making rod and tube of small diameter. In the background, a vertical ram extrusion press (courtesy of STEATIT-MAGNESIA A.G., "STEMAG", Lauf-Pegnitz)

sintered to density in air-atmosphere coal- or gas-fired *chamber* kilns (Figs. B 12-8, B 12-8A). In many cases they are protected by fireclay capsules from the direct effects of the heating flames and mainly from the flue dust of coal-fired kilns (Fig. B 12-8B). Gas and electrically fired *tunnel* kilns are also coming into operation (Fig. B 12-9), especially for firing small parts. Electric furnaces have proved necessary mainly for firing material required to have low electrical losses and with readily reducible additives, and also for materials of small sintering range, since electric furnaces can have better temperature control. Up to 1450°, high-temperature furnaces with an oxidizing atmo-



C

[12.1]

Fig. B 12-4 Casting ceramic bodies (HESCHO)

A hollow casting: the porous mold powerfully extracts water from the pulp so that a solid layer of even thickness forms on the mold wall, the external shape corresponding to the internal shape of the mold
B core molding: to avoid cavities, pressure casting is also employed; the internal shape of the piece corresponds with that of the core
C core molding process

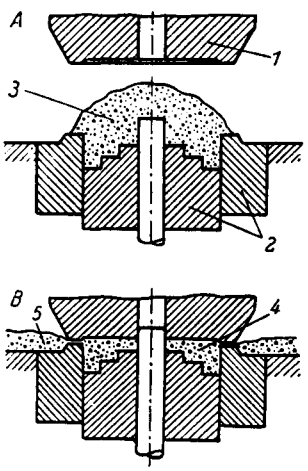


Fig. B 12-5 Wet molding of ceramic pressings (schematic)

A filling, *B* pressing
1 upper die; *2* pinching die; *3* excess starting batch; *4* molded batch; *5* pinched-off material

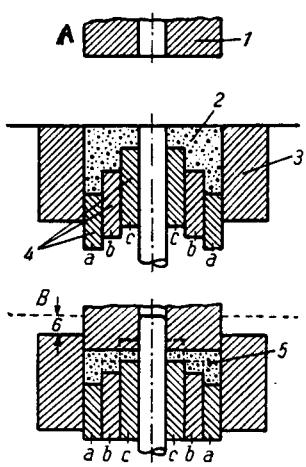


Fig. B 12-6 Dry molding of ceramic pressings (schematic) (HESCHO)

A filling, *B* pressing
1 upper die; *2* measured quantity of starting batch; *3* mold sleeve; *4* section mold; *5* compressed batch; *6* sleeve displacement during molding

[12.1]

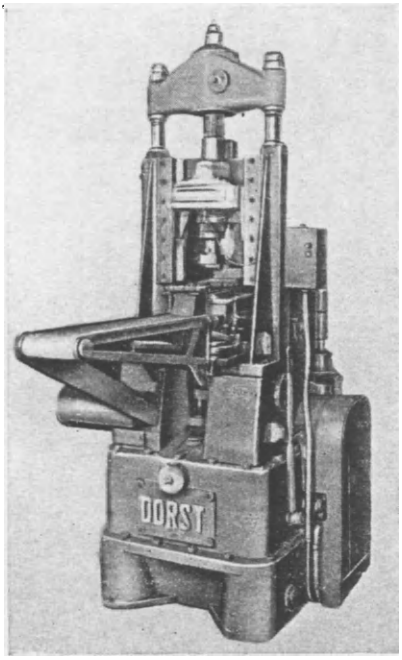


Fig. B 12-6A Hydraulic dry molding press, semi-automatic (used by STEATIT-MAGNESIA A.G., Lauf-Pegnitz; press made by DORST-KERAMIK MASCHINENBAU, Kochel am See/Oberbayern)

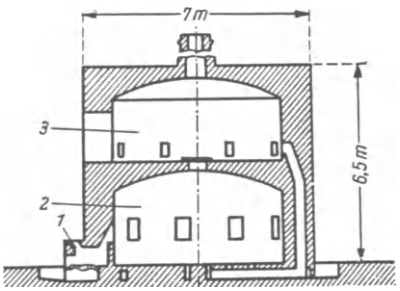


Fig. B 12-8 Section through a two-story cylindrical kiln, coal-fired (courtesy of HESCHO)

1 firing; *2* finishing burn chamber (max. 1450°); *3* chamber for first bake (max. about 850°)

Fig. B 12-7 Drying chamber for ceramic pressings; air feed temperature and moisture content can be regulated (courtesy of HESCHO)

Fig. B 12-8A View of a kiln with ceramic components in protective containers. Before firing begins, the kiln opening seen here is sealed with a brick wall, in which small viewing ports permit observation of the firing by means of Seger cones (courtesy of PHILIPS, Eindhoven) (IJDENS)

sphere generally have silicon-carbide heater rods, but these rapidly decarbonize above 1500°. Therefore, for temperatures up to 1600°, heaters have recently been developed based on molybdenum disilicide ($MoSi_2$) (KIEFFER), and sold under the name "Kanthal Super". Still higher temperatures (somewhat over 2000°) in an oxidizing atmosphere can be reached only by gas-fired kilns, in particular surface-combustion kilns. (See, e.g., RYSCHKEWITSCH.)

[12.1]

Fig. B 12-8 B Introducing pre-dried ceramic tubes into protective casing prior to firing. Such tubes are normally dried and fired freely suspended to guard against warping (courtesy of PHILIPS, Eindhoven) (IJDENS)

The firing temperature of silicate ceramics lies mostly between 1300° and 1500°, depending on composition of the starting material which determines the sintering and softening temperature, and also, in the case of deliberately porous ceramics, the desired porosity.

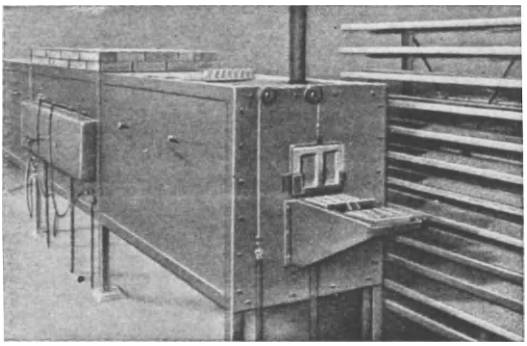
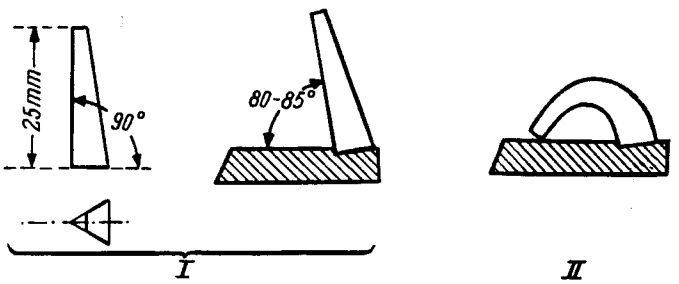


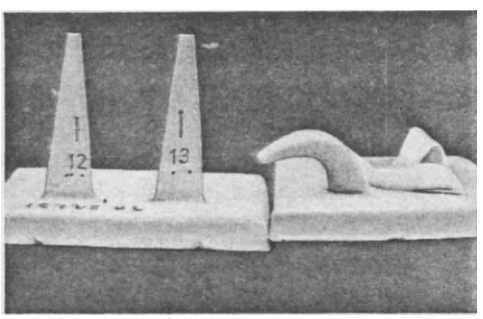
Fig. B 12-9 Electric tunnel kiln for small ceramic parts (courtesy of HESCHO)

Since the piece shrinks linearly during firing by 2–30%, depending on the material and the mode of manufacture, the tolerances attainable with fired ceramics are generally not very tight. Without further working at intermediate or final stages, thrown or cast bodies have tolerances of about $\pm$3–5%; wet or extruded pressings have about

$\pm$2–3%, and dry pressings $\pm$1–2%. See, e.g., DIN Norm 40 680/9.54 for permissible tolerances for mass-production of silicate ceramics without finish grinding.

Sometimes a prefiring ("first bake") at 800–900° takes place before the actual firing ("finishing burn"); see Fig. B 12-8. Since hardness and strength of the pressing increase only gradually with temperature and duration of firing, biscuit-ware baked at moderate temperatures can be readily finished with special steel tools ("white machining") by chip-cutting methods (more correctly "dust-cutting") used for metals, i.e. turning, milling, drilling and thread-cutting. This has the great advantage that the pressing
[12.1] before the first bake need only be roughly to shape, and is machined to final dimensions only after the first bake. In this way, much greater precision can be achieved, since the





III

Fig. B 12-10 Seger cones and their application

I Seger cone as per DIN 51 063/12.54, dimensions and mounting
II Cone being heated to the so-called "point of fall", reached as soon as the tip just touches the refractory base by bending along the short edge
III temperature-measuring set-up with two cones, No. 12 (1350°) and No. 13 (1380°), on a base plate; *left*: before firing; *right*; after setting the furnace temperature to about 1360° (KLÄY)

drying shrinkage, which experience has shown to be very hard to predict, plays no part, and the reasonably constant contraction due to the finishing burn can be calculated with fair accuracy.

Furnace temperatures in firing can be monitored either by thermocouple or the "Seger cones", three-sided pyramids about 2.5–6 cm high and made of clay. The pyrometric cones are composed of a series of mixtures of glazes, each mixture having a certain melting point. On average, M.P. rises by 20° for every cone number; thus cone tilting (Fig. B 12-10) indicates that a certain temperature has been reached in the kiln. This indication, however, is only accurate to $\pm$15°. Table T 12–2 contains approximate melting temperatures for cones of different SK number (SK = Seger Kegel), and Table T 12–3 the approximate temperature equivalents of the American pyrometric cones (see also ORTON). Compared with thermels, cones have the advantage of actually measur-

TABLE T 12-2. SEGER CONE (SK) NUMBERS AND APPROXIMATE MELTING TEMPERATURES (T) OF THE CONES

SK NO.	T (°C)	SK NO.	T (°C)	SK NO.	T (°C)
022	600	4a	1160	34	1750
021	650	5a	1180	35	1770
020	670	6a	1200	36	1790
019	690	7	1230	37	1825
018	710	8	1250	38	1850
017	730	9	1280	39	1880
016	750	10	1300	40	1920
015a	790	11	1320	41	1960
014a	815	12	1350	42	2000
013a	835	13	1380		
012a	855	14	1410	Red Seger cones	
011a	880	15	1435		
010a	900	16	1460	010	900
09a	920	17	1480	09	930
08a	940	18	1500	08	970
07a	960	19	1520	07	1000
06a	980	20	1530	06	1020
05a	1000	26	1580	05	1040
04a	1020	27	1610	04	1060
03a	1040	28	1630	03	1080
02a	1060	29	1650	02	1100
01a	1080	30	1670	01	1120
1a	1100	31	1690	1	1140
2a	1120	32	1710	2	1155
3a	1140	33	1730	3	1170

[12.1]

ing $\int T(t) \cdot dt$, where T = temperature and t = time; this gives a more accurate picture of the effects of heating on the ceramic body during the whole firing process.

From the chemico-physical standpoint, ceramic firing is a very intricate process full of individual processes and reactions of which the following may be the main ones:

1. First, the mechanically held water and then the water of crystallization is removed, resulting in loss of plasticity, contraction, and gain in strength. Volume shrinkage is also a feature of the processes (2)–(6) below.

2. All combustibles (C, S) are burned off; carbonates, sulfides and sulfates (e.g. those of Ca, Mg, Fe, etc.) break down to oxides, giving off decomposition and combustion gases.

3. Modifications in crystal structure occur; e.g., the main components of ordinary porcelains (Al_2O_3, SiO_2) recrystallize to mullite ($3\,Al_2O_3 \cdot 2\,SiO_2$) or those of steatites (see further below), i.e. soapstone ($3\,MgO \cdot 4\,SiO_2 \cdot H_2O$) and feldspar ($K_2O \cdot Al_2O_3 \cdot 6\,SiO_2$), form a new crystal constituent "enstatite" ($MgO \cdot SiO_2$).

4. The fusible additives (fluxes) melt and dissolve unfused crystalline material, resulting in two types: those that form glassy phases and then with other materials produce more glass (e.g. lead oxide and borax); and those that are themselves ceramic oxides, but readily form glasses via eutectic compounds (e.g. oxides of Mg, Zn, Ba). On the other hand, the glassy components can form new crystallites by devitrification.

TABLE T 12-3. APPROXIMATE TEMPERATURE EQUIVALENTS FOR AMERICAN PYROMETRIC CONES (PER ASTM DESIGNATION C 24-46)[1] (FAIRCHILD, KOHL)

CONE NO.	P. C. E.[2] (°C)	CONE NO.	P. C. E.[2] (°C)	CONE NO.	P. C. E.[2] (°C)
022	605	02	1125	19	1520
021	615	01	1145	20	1530
020	650	1	1160	23	1580
019	660	2	1165	26	1595
018	720	3	1170	27	1605
017	770	4	1190	28	1615
016	795	5	1205	29	1640
015	809	6	1230	30	1650
014	830	7	1250	31	1680
013	860	8	1260	32	1700
012	875	9	1285	33	1745
011	905	10	1305	34	1760
010	895	11	1325	35	1785
09	930	12	1335	36	1810
08	950	13	1350	37	1820
07	990	14	1400	38	1835
06	1015	15	1435	39	1865
05	1040	16	1465	40	1885
04	1060	17	1475	41	1970
03	1115	18	1490	42	2015

[12.1]

[1] The values hold good for temp. rise rates of 150 °C/hr for cone no. 022 to 20, 100 °C/hr for 23 to 38, and 20 °C/hr for 39 to 42.

[2] P. C. E. = *P*yrometric *C*one *E*quivalent, also called softening temperature.

Fluxes are important for making non-porous, dense ceramics and for lowering the sintering temperature, but they have the effect that the ceramic batch is more or less viscous throughout the firing process so that undesired deformation of the piece can occur easily. In some circumstances supporting devices will counteract this, and it is helpful to shape the piece to be as mechanically stable as possible.

5. The fluid components fill a large fraction of the pores remaining after water and decomposition gases have escaped.

6. Small crystallites grow larger by agglomeration; this is the main process in sintering pure metal oxide ceramics (see 12.6).

7. The new structure produced by firing gives the piece the greatest portion of its mechanical and electrical strength; typical examples of this are:

(a) porcelains (with 15–20% alumina): the glass phase ($Al_2O_3 + SiO_2$ + alkalis), mullite crystals (rarely corundum) and excess SiO_2 in the form of α-quartz,

(b) soapstones: enstatite crystals formed during firing, which primarily give the pressing its excellent electrical properties.

8. Too low a firing temperature (under-firing) leads to incomplete development of some of the reactions described, and thus lower density and strength. Over-firing leads to deformation and bubble formation (swelling of gas-filled pores sealed off by the flux).

High-quality vacuum-tight sintering therefore requires fairly close approach to the upper limit of the available sintering range (e.g. up to about 5° below deformation point of Forsterite and zircon ceramics); this in turn requires a long, well-regulated electric kiln, which must be run for some time before actual firing takes place so as to achieve constancy of temperature distribution.

It is now clear that all in all even with very fine-grained starting materials, the end result of the firing is a solid siliceous, oxide ceramic made up of a discontinuum of

[12.1]

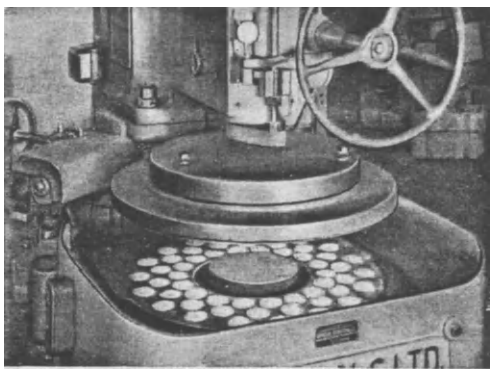


Fig. B 12-10 AI Plane-parallel machine grinding of fired ceramic disks between two counter-rotating flats (courtesy of PHILIPS, Eindhoven) (IJDENS)

Fig. B 12-10 AII Grinding machine for two-sided mass-production grinding of fired ceramics (courtesy of STEATIT-MAGNESIA A.G., Lauf-Pegnitz)

The abrasive in the form of an aqueous suspension is introduced between the pair of counter-rotating cast-iron wheels through holes in the upper wheel

crystals, glass and pores (see, e.g., Fig. B 12-35A to D); dense bodies are produced if the firing temperature is high enough, porous shards if the temperature is low or also if suitable additions are made. An example of the latter is powdered, dead-burned material of low-flux clay (grog) added to form an artificially porous structure. Dense ceramics also contain many internal pores (see Fig. B 12-35A), but these pores are not connected with one another ("closed porosity") so that water take-up, a measure of "open porosity" or apparent porosity, is almost nil. (See also 12.2.I.)

The resulting ceramic bodies can exhibit preferential arrangement of material in zones or layers, brought about by the kind of forming process used; for example, in extruded bodies layering is similar to that of flowing liquids.

12.1.V. *Finish Machining*

Once high-temperature fired, the hard ceramic piece can generally be machined only by grinding with SiC or diamond wheels and diamond powder. Exceptions are some fine-grain specialities like Ergan and similar ceramics of Group 240, DIN Norm 40685 (see Tables T 12–10D, 12–11D, also 12.3.IIIb), Alsimag 222 (Table T 12–10, A1) and Porolite (Table T 12–11C). Since the finishing procedure is costly, the manufacturer of precision ceramics should limit himself to a slight degree of corrective finishing. This finishing can only be regarded as economical in special cases, but the same precision can be attained as for metallic materials. Recently, special machines have succeeded in considerably reducing the cost of making precision ceramics; with simple plane or

[12.1]

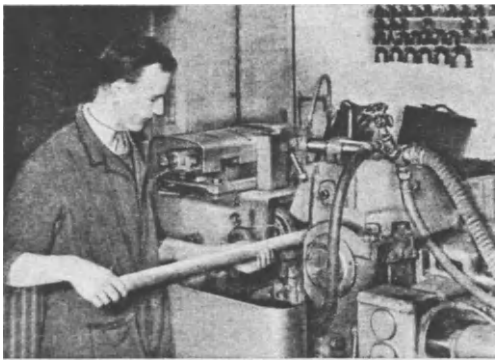


Fig. B 12-10B Cylindrical grinding of fired ceramic rod or tube on the "centerless grinder" (courtesy of PHILIPS, Eindhoven) (IJDENS)

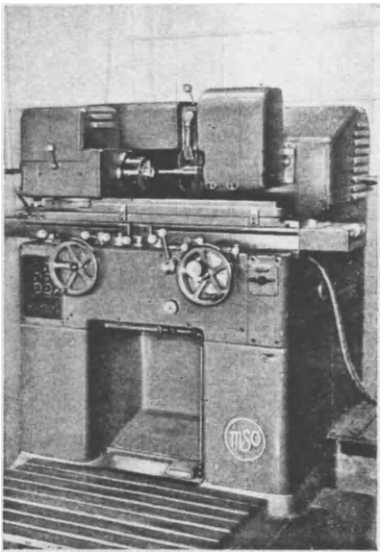
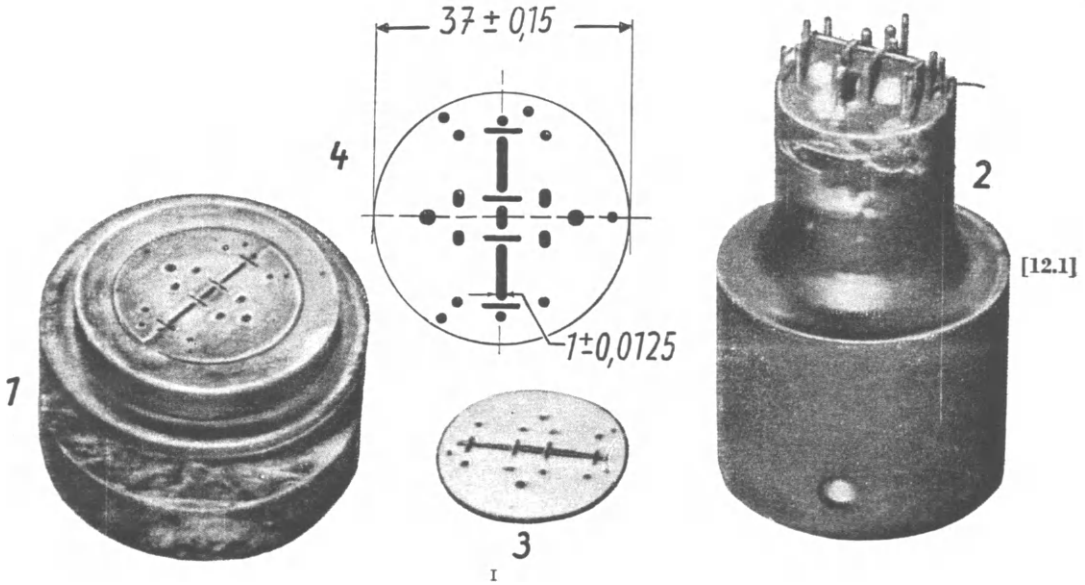


Fig. B 12-10C Machine for surface finish grinding of the inner hollows and circular holes of fired ceramics (from the production line of STEATIT-MAGNESIA A.G., Lauf-Pegnitz)

cylindrical grinding, a precision of ± 0.01 mm or better can be had with tolerable outlay (WILLIAMS; see also 12.5, e.1).

For simple plane grinding, one can use rotary cast-iron plates and a feed of water plus silica sand as abrasive, or silicon-carbide wheels; for plane-parallel grinding, reversing or rotary tables (Fig. B 12-10 AI and AII); for simple external cylinder grinding, cylindrical grinders. Threads, spirals and grooves can be cut on the lathe. Centerless grinding is used particularly for shafts and tubes (Fig. B 12-10B). With large diameter pieces, this is preceded by grinding between centers. For precision grinding of internal surfaces and round holes, the precision-ceramic industry has available high-



[12.1]

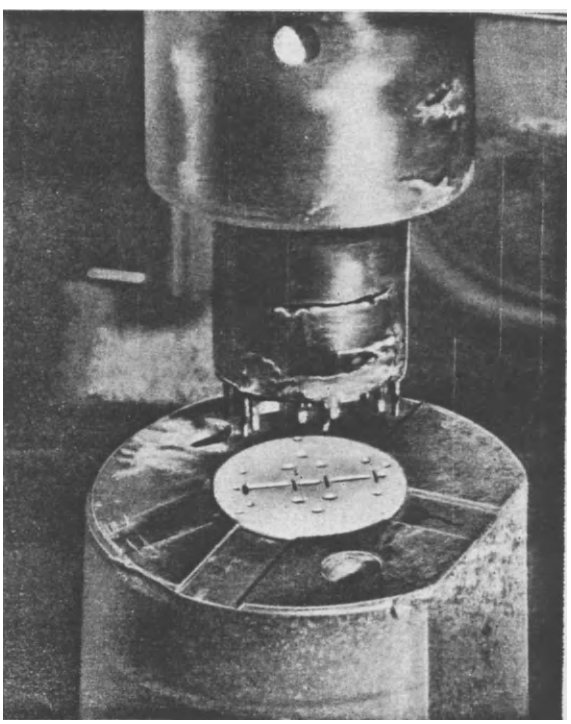


Fig. B 12-10D Ultrasonic drill for ceramic disks

I detailed components
Drilling matrix (*1*) and male die (*2*) for ultrasonic impact-grinding of precisely profiled holes in Al_2O_3 support plates (*3*); (*4*) typical tolerances (dimensions in mm) II overall set-up (courtesy of THE C-MAR CORP., Manasquan, N.J., USA) (cf. also Fig. B 10-162A)

capacity, specially designed machines, a practical example of which is shown in Fig. B 12-10C. Holes are drilled in fired parts on internal grinders or drilling machines by means of diamond or cemented carbide tools. Larger holes in ceramic plates can be drilled as in the case of glass with Cu tubes and SiC or diamond dust. Where possible however, accurate holes and close-tolerance profiles should be avoided. It should be noted that threads in fired parts can be ground only with relatively coarse pitch and large-radius corners to avoid edge fracture; external threads, 0.75 mm pitch, down to 6 mm dia., internal threads only from 25 mm dia. up.

[12.1] The ultrasonic method has proved to be very advantageous, especially for drilling and slotting ceramic plates; it has already been described in 10.3.VII (esp. Fig. B 10-162A). Figure B 12-10D shows a drill for impact grinding of profiled holes for distance pieces made of high-alumina ceramic for electron tubes (see also [4]ANON.).

Fig. B 12-11 Glazing of fired piece-parts by enamel spraying (courtesy of HESCHO)

Some ceramic bodies must remain vacuum-tight, for example ceramic tubing for envelopes of electron tubes (Fig. B 5.6-10); the "firing skin" must not be ground off on *both* sides. This skin is formed on the ceramic during firing and even in the case of ceramics low in glassy phase constitutes a sort of molecular, sealing, enamel-layer whose presence can be inferred also from the effect it has on the strength of the body. Therefore, where possible, such bodies are only ground in places which are to be metalized later, and all other regions are left undisturbed as far as can be.

12.1.VI. *Glazing*

Ceramics can be enameled to ensure tightness, improve volumetric resistivity by reducing water take-up (closing surface pores), and also to increase mechanical strength by reducing notch effect at the surface. The technique (10.6.II) involves spraying (Fig. B 12-11) or dipping, then heating the glaze layer, which must be resistant to atmospheric corrosion. The glaze α should be less than that of the base ceramic so as to put the thin glaze under compression rather than tension after cooling, since the compressive strength of glass is about 10 times the tensile (10.2.I). One can distinguish two types of glaze:

(a) *Hard glazes* (feldspars, porcelains). They are applied to the fired or biscuit-ware (e.g. porcelain or steatite) and then sintered with the shard in the "sharp fire" or finishing burn. Figure B 12-35E shows a typical polished section of such a glaze on a porcelain shard.

(b) *Soft glazes* (lead borate glazes). These are mostly produced from aqueous suspensions of fine glass powder of composition $SiO_2 + B_2O_3 + PbO + Al_2O_3$ (see BUDNIKOW, LIEBSCHER, and NEUBAUER for recipes). These are applied to the fired (sintered) shard which then undergoes a second firing at lower temperature, usually only 850–1100°. [12.2]

For many vacuum purposes, such glazes are of little value since they make it more difficult to degas internal components and, in the case of soft glazes, lower the temperature rating of the component because of the low M.P. of the glaze and its (generally) high dielectric loss. Besides, they can rarely be used on components with precision-ground finish so often employed in vacuum technique.

12.2. Properties of Silicate Ceramics; Methods of Measurement

(ASTM, BSI, ČSN, DIN-Norm, VDE)

Before proceeding in detail with special types of silicate ceramics and their properties, a short discussion should first be given on methods of property measurement, where they differ from those for other insulators (especially glass) used in vacuum work. Further, we should discuss the general relationships which hold for ceramics, especially at high temperature and frequency.

12.2.I. *Apparent Density, Porosity, Water Take-up*

Almost all ceramics contain, as stated, a large number of pores, even very dense-sintered bodies, whose closed pore volume still amounts to 2–6%. For this reason it is customary to give the apparent density (g/cm³) inclusive of pore volume. This lies between 1.8 and 3.9 for technical silicate ceramics. One only speaks of a ceramic being oporous ("open" or "apparent" porosity) when the plurality of microscopic pores is interconnected right up to the surface of the body, producing a degree of gas and water permeability. This is determined either by measurement of the water-absorption WA, or absorbency SF ("Saugfähigkeit"); refer also to VDE 0335 on this point.

The water absorption WA is the weight per cent of water that a body can absorb at saturation, referred to the dry weight of the body, and is defined by

$$\mathrm{WA} = 100\,\frac{G_w - G}{G}\,(\%),$$

where G is the weight of the freshly broken pieces of the ceramic test-body (about 50 g, with at least 25% break-up surface) after careful drying for 3 hr at 150° in an oven and cooling in a desiccator; G_w is the weight of the pre-evacuated pieces after 12 hr standing in distilled water followed by surface wiping (VDE 0335). More exact results are obtained by heating the pieces in distilled water up to B.P. in 30 min, boiling for 2 hr, and allowing the pieces to cool in the water for 24 hr.

From the WA value the corresponding open porosity is calculated as

$$P_0 = \mathrm{WA}\,\frac{\gamma}{\gamma_w}\ (\%),$$

where γ is apparent density and γ_w the density of the water (both in g/cm³).

Absorbency SF means the ability of a fired ceramic to take into its structure a certain quantity of fluid; this is the VDE 0335 definition. To determine SF, pieces of the ceramic under test are broken off and held for 4 hr in an alcoholic solution of aniline dye (1 g fuchsin in 100 ml methanol) at 150 atm. In the case of dense-fired ceramics, the crushed [12.2] pieces should show no penetration of dye below the surface of the shard. The pressurized fuchsin test is only significant with shards whose WA has been found to be less than 1%, and is only qualitative.

Knowledge of the porosity is not only of importance for assessing the tightness of vacuum envelopes made of ceramic, and ease of degassing internal parts (which is improved by high porosity, the converse of the vacuum tightness situation); it is also a means of evaluating thermal shock resistance, thermal conductivity, and surface resistivity. Table T 12–11 contains WA data for commercial ceramics. High-porosity ceramics (P_0 = 20–40%) are used in vacuum work for restricting flow in gas inlet valves (Figs. B 12-59, B 12-60). Medium-porosity ceramics (P_0 2–15%) are used for high-temperature insulators, while dense-fired ceramics have mainly high-voltage and vacuum envelope applications.

12.2.II. *Softening Temperature*

Since silicate ceramics consist of mixtures of crystalline metal oxides and metal silicates with a more or less high glass-phase content, they have a rather indefinite M.P., just as glass does. At elevated temperatures they gradually soften and deform under dead weight or under the weight of attached components. Unlike glass, they cannot be thermoplastically formed because of their high content of crystalline constituents.

The softening point is determined either by the above-mentioned cone fall point KFP (Table T 12–2) or as T_{soft} (Table T 12–3). The safe temperature of continuous heat for porous ceramics generally lies 200–300° below T_{soft}; with dense-fired ceramics, containing large amounts of glassy binder, 400–500° below the cone fall point. The T_{soft} under load is usually found by applying compressive loading (e.g. 2 kg/cm²) and heating at a rate of 5°/min (see DIN 1064), or by equipment like that in Fig. B 10-10. When using ceramics as heat-conducting supports it should be noted that contact with metals may form low-melting compounds which can lead to considerable reduction in maximal operating temperature. An example of this is contact between high-alkali ceramics and the chromium oxide on NiCr heater wires.

12.2.III. *Vapor Pressure*

Technical ceramics have a negligibly low vapor pressure up to 800°, about 10^{-6} Torr or less. There are no direct measurements available, but this fact can be deduced indirectly from Figs. B 11-5B and B 12-61, where the SVPs of the main components of silicate ceramics (SiO_2, MgO, Al_2O_3, ZrO_2, BaO, CaO) are given as temperature functions.

12.2.IV. *Mechanical Properties*

Statements made about glass (10.2.I) are essentially valid for ceramics under load, but with the difference that the strength values vary considerably with composition and porosity. Like glass, ceramics are brittle, that is, fracture follows overload at once without the elongation or flow that accompanies metallic fracture. Figure B 12-12 shows how this behavior contrasts with that of metals. As with technical glasses, the compressive strength of ceramics is greater than tensile or bend strengths by factors of 10–20 (Table T 12–11) and is of the same order as that of metals (cf. Fig. B 10-4). Where ceramic-metal joints are concerned, as in vacuum-tight brazing of a metal ring to a surface-metalized ceramic, it is essential always to arrange that the ceramic is under compressive stress, and the metal under tensile and possibly bend stress (see also Chapter 32). [12.2]

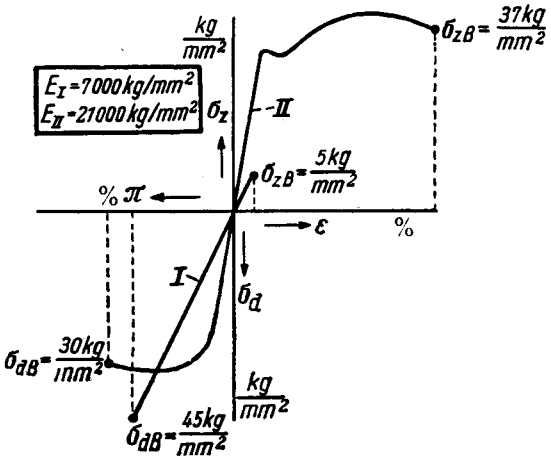


Fig. B 12-12 Stress–strain curve of a ceramic. Curve *I* for hard porcelain (DIN type 110) compared with a steel in curve *II* (steel DIN type St 37,11)

σ_z = tensile stress; σ_{zB} = tensile strength σ_d = compressive stress; σ_{dB} = compressive; strength; ε = strain; π = compressive strain; E = Young's modulus

The parameters usually measured to indicate the chief mechanical properties of technical ceramics are tensile and compressive strengths, and bend and impact strengths. Strength values, as usual, are referred to area of cross-section, and unlike metals, the values for dense ceramics are functions of section area (Fig. B 12-13) and also of shape factor; above 30% porosity, strength is generally unrelated to area of section. The dependence on shape apparently arises from uneven stress distribution across the section, contrary to the hypothesis on which strength calculations are made. At all events, the result of these dependences is that all data in the literature are based on definite test-body dimensions laid down in test standards (see, e.g., VDE, ASTM).

The strength of ceramics is increased by glazes which have smaller αs than the ceramic and therefore are under compression after melting and cooling.

There are no reliable measurements for the strengths of commercial silicate ceramics as temperature functions; however, see 12.6 (Pure Oxide Ceramics); Figs. B 12-62, B 12-62B, B 12-63.

12.2.V. *Hardness*

A characteristic of ceramics is great surface hardness. Since their brittleness, as with glass, prevents measurement of Rockwell or Brinell hardness (the usual method with metals and plastics), Knoop or only scratch hardness can be determined. The latter is based on the Mohs' scale (Table T 12–4). Two materials are said to have the same Mohs' hardness when neither will scratch the other; if a mineral on the scale is scratched by

[12.2]

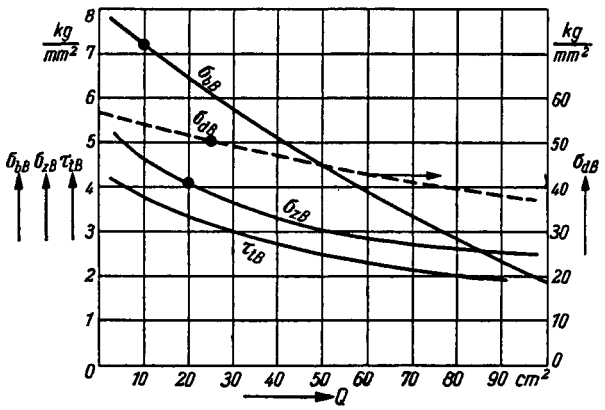


Fig. B 12-13 Strength properties of hard porcelain as a function of cross-sectional area of test-piece ([1]ESPE)

σ_{zB} = tensile strength; σ_{dB} = compressive strength; σ_{bB} = bend strength; τ_{tB} = torsion strength. The left-hand ordinate applies to solid curves, and the right-hand one to dashed curves

the ceramic, and the ceramic is scratched by the next hardest mineral, the Mohs' hardness number lies between that of the two minerals. In the Knoop test (KNOOP, LYSAGHT), a pyramidal diamond point of fixed shape, loaded with 25–50 g (L), is driven into the test-body; the projected area (A) if the impression is measured by microscope,

TABLE T 12–4. MOHS' HARDNESS AND KNOOP HARDNESS NUMBERS COMPARED

MOHS' HARDNESS SCALE NUMBER	TYPICAL REPRESENTATIVE MATERIAL	KNOOP HARDNESS NUMBER	KNOOP HARDNESS EXAMPLES FOR CERAMICS
1	Talc	—	—
2	Gypsum or rock salt	32	—
3	Calcite	135	—
4	Fluorspar	163	—
5	Apatite	395 (∥ 360, ⊥ 430)	—
6	Orthoclase	560	Hard porcelain 600
7	Quartz	750 (∥ 710, ⊥ 790)	—
8	Topaz	1250	—
9	Corundum	1635	Alumina 1600
10	Diamond	5500–6950	Boron carbide 2230

and the hardness number calculated by the formula

$$H_{Kn} = L\,(kg)/A\,(mm^2).$$

A conversion table for Mohs' and Knoop numbers is given in Table T 12–4. Generally, Mohs' numbers for ceramics lie between 6 and 9 (Table T 12–11).

12.2.VI. *Thermal Expansion Coefficient*

Linear expansion is usually determined on 4 mm dia. rods, ground to 50 mm length exactly, in a differential dilatometer. The technique of measurement is the same as for technical glasses (Figs. B 10-23 to B 10-26, and related text). Figure B 12-13A shows a fully-automatic unit specially suited to recording ceramic characteristics up to 1500°. In contrast to glass, the expansion curves up to T_{soft} are almost linear, of small gradient, [12.2]

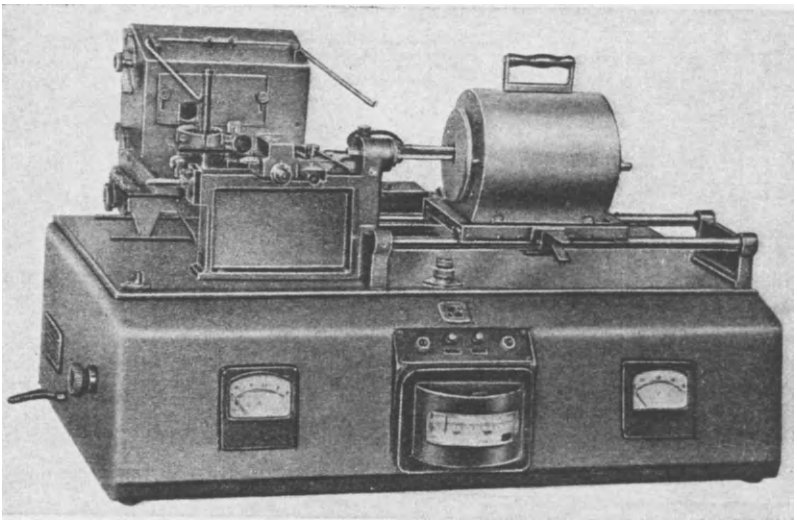


Fig. B 12-13A Fully-automatic dilatometer for photorecording thermal expansion characteristics of solids, especially ceramics, up to 1500°, with temperature rise adjustable from 1–10°/min (made by GEBR. NETZSCH, Selb in Bayern)

and reversible: this is because there is no transformation point. Rarely, there are a few slight (reversible) inflexions caused by recrystalization of certain constituents in the ceramic. The αs of technical ceramics lie between $10–120 \times 10^{-7}$/°C. Table T 12–5 and Fig. B 12-14 give a survey of this parameter, and Fig. B 10-40 gives comparisons with other materials. Figures B 12-33 and B 12-34 give other commercial ceramic expansion characteristics.

12.2.VII. *Thermal Shock Resistance and Thermal Stress Resistance*

What has been said about thermal shock resistance of technical glasses in 10.2.V holds in all essential respects for silicate ceramics. In this case also, the expansion coefficient is crucial: the smaller α, the higher thermal shock resistance. Thermal conductivity and tensile strength also have some influence on thermal shock resistance.

TABLE T 12-5. MEAN LINEAR THERMAL EXPANSION COEFFICIENT α_m OF SOME TYPICAL CERAMICS, IN ASCENDING ORDER
(For ceramics with negative α, see, e.g. [2]SMOKE)

TYPE OF CERAMIC	α (20–700 °C) 10^{-7}/°C
Types containing cordierite	22–28
Hard porcelains	35–55
Ceramics containing zircon	40–60
High-alumina ceramics	65–80
[12.2] Steatite	70–102
Forsterite	105–112

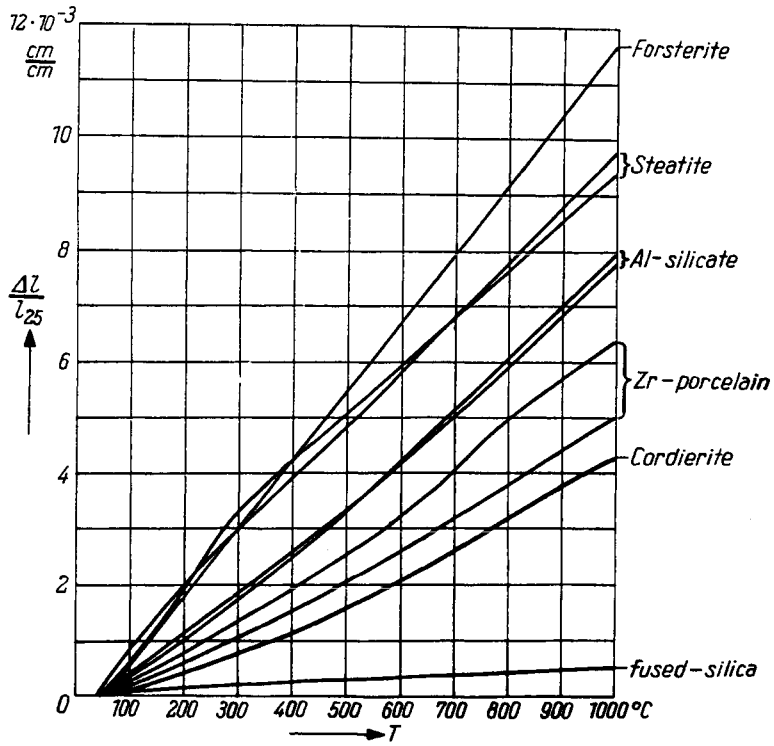


Fig. B 12-14 Thermal expansion characteristics of some typical ceramics. For more characteristics of commercial ceramics see Figs. B 12-33, B 12-34, B 12-38, B 12-40, B 12-43, and B 12-77

Rapid cooling of the surface of solid ceramics gives rise to tensile stress, which the ceramic cannot easily support because tensile strength is low compared with compressive. Therefore, sudden chilling is always a greater hazard than sudden heating. As with glass, thermal shock resistance is determined by quickly immersing the test-body in cold water after heating in an air-atmosphere furnace, and the temperature is raised at each test by small intervals (10° or so). This is repeated until dabbing the test-piece with an alcoholic solution of fuchsin (12.2.I) first shows up cracks. The difference in temperature between

TABLE T 12-6. APPROXIMATE THERMAL SHOCK RESISTANCE VALUES FOR TECHNICAL CERAMICS WITH DIFFERENT EXPANSION COEFFICIENTS, ARRANGED IN DESCENDING ORDER

TYPE OF CERAMIC	α (20–700 °C) 10^{-7}/°C	THERMAL SHOCK RESISTANCE (°C)
Lithium ceramics (spodumenes)	—ve	400–1200(2)
Cordierite ceramics	16–17	270–275(2)
	10–20	240–326(1)
Porous ceramics	40–60	220–300(1)
Zircon porcelains	40–60	210–280(2)
Hard porcelains	40–60	160–200(1)
High-alumina ceramics (alumina)	56	180–210(2)
	60–80	150–160(1)
Ordinary steatite	70–100	80–150(1)
Forsterite	105–112	70–110

[12.2]

(1) VDE test-body.

2) Test-body 12.5 mm dia., 250 mm long.

furnace and quenching water at the point of initial cracking is a measure of thermal shock resistance. Test-body dimensions are standardized: for example, the VDE 0335 specification calls for a solid cylinder, 25 mm dia., 25 mm length. Porous ceramics show much higher thermal shock resistances than dense-sintered bodies of the same chemical composition. However, since a porous surface makes it difficult to detect cracks by repeated fuchsin applications, thermal shock resistances are tested by measuring

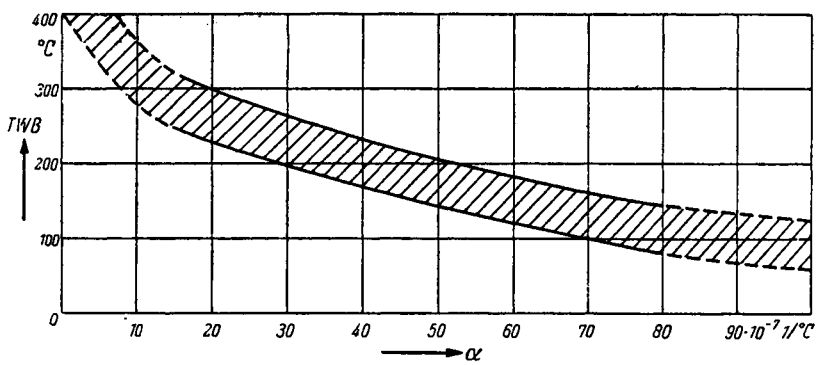


Fig. B 12-15 Rough plot of the dependency of thermal shock resistance (TWB) on thermal expansion coefficient α of technical ceramics

bend strength of standardized rods (VDE spec. 10 mm dia., 120 mm long), and this is repeated after heating and quenching in cold water. The quenching ΔT that causes reduction of bend strength to two-thirds the original value is the thermal shock resistance: the original value is measured on equi-dimensional bodies of the same type of ceramic without heating and quenching. Table T 12–6 is a collection of thermal shock

resistance values for various types of ceramic; Fig. B 12-15 shows very roughly the relation between α and thermal shock resistance for technical ceramics.

Besides thermal shock resistance, thermal stress resistance (cf. 10.2.VI) should be considered. This property is the ability of a ceramic to withstand without fracture temperatures which are invariant with time but spatially variant (i.e. continuous temper-

[12.2]

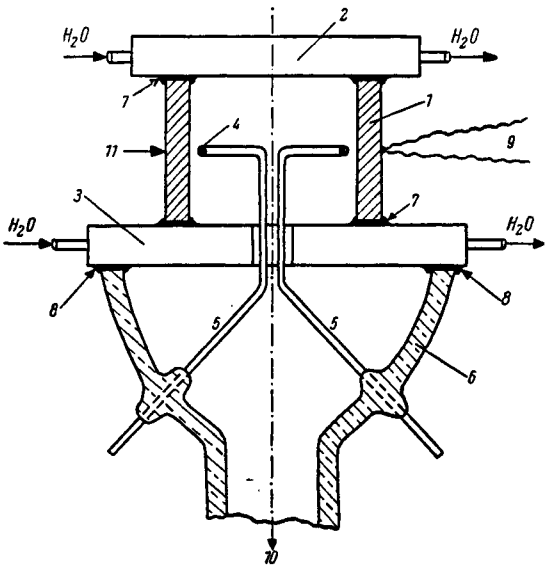


Fig. B 12-15A Set-up for determination of thermal stress resistance of ceramic tubes (PREIST)

1 ceramic tube, length 25–50 mm, I.D. *ca.* 40 mm, wall 1.25–3.1 mm; *2* water-cooled cover-plate; *3* water-cooled baseplate with central hole; *4* heater loop of W (wire diameter *ca.* 3 mm, length *ca.* 75 mm) about 2 mm from wall and brazed with Pt to leads *5* made of Mo wire (6 mm); *6* glass bell-jar; *7* and *8* joints made with vacuum cement; *9* iron-constantan thermel, joined at one point by cement to the outer cylinder wall; *10* port to a rotary fore-pump for 10^{-2} to 10^{-3} Torr operation

Power is applied to the heater loop, and slowly raised; the temperature of the hottest zone (*11*) of the tube at which the tube fractures (air inlet) is determined, and this is a relative measure of thermal stress resistance (cf. Fig. B 12-15B)

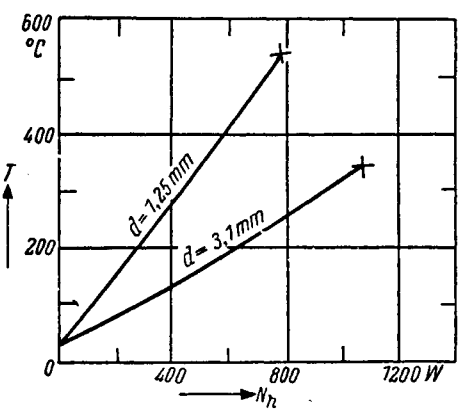


Fig. B 12-15B The temperature T of the hottest part of high-alumina ceramic tubes of different wall-thicknesses d is shown as a function of power N_h in a heater loop. The measurement is carried out by means of the device shown in Fig. B 12-15A. The T value (+) at the end of each curve is a relative measure of thermal stress resistance

ature gradients); this applies particularly to cases where the ceramic is used as a vacuum-tight envelope for an electron tube. In most constructions of this type, the ceramic is in the form of a cylindrical tube metalized at the ends and provided with relatively cool metal connecting terminations. For this reason, thermal stress resistance is determined on a cylindrical evacuated tube of fixed length and wall, whose central zone is heated by radiation from a hot internal electrode (e.g. a heated loop at a constant distance from

the tube wall) while the cemented metal closure caps at the ends are water-cooled (Fig. B 12-15A).

The following qualitative determinations were able to be made on high-alumina tubular ceramics, 89–100% Al_2O_3, walls 1.25–3.1 mm (PREIST): grinding the tube surface reduces thermal stress resistance probably because of surface fissures. Heating for $^1/_2$ hr in forming gas at 1425°, followed by slow cooling (better still, rapid cooling in air) much increases thermal stress resistance; the effect is less marked for very high-alumina ceramics than for those with less Al_2O_3 (i.e. more SiO_2—CaO—MgO content). [12.2]

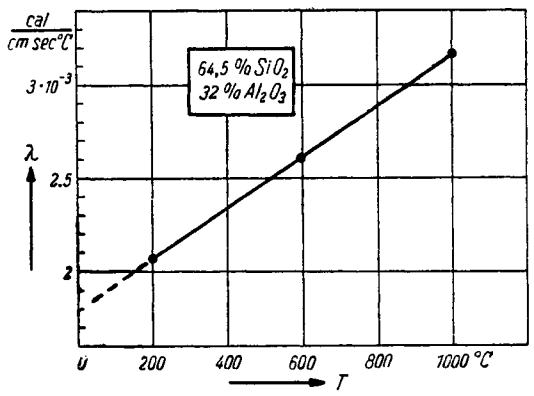


Fig. B 12-16 Thermal conductivity λ of a porous aluminium silicate (firebrick) as a function of temperature T (ENDELL)

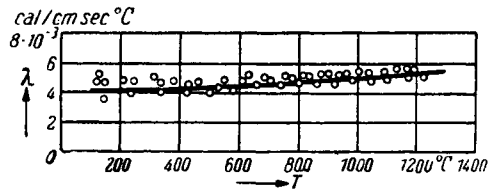


Fig. B 12-16A Thermal conductivity λ of an electrical porcelain as a function of temperature T ([1]KINGERY)

Thermal stress resistance falls with increasing wall thickness d of the tested tube (measured up to $d = 3.1$ mm); in spite of this, a tube with thick walls will take a higher local wattage rating (Fig. B 12-15B), since the temperature gradients between hot central zone and cooler ends are lower because of the higher axial thermal conductance produced by thicker walls. Thermal stress resistance of high-alumina ceramics is greater than that of steatities and forsterite, but is exceeded by fused silica and sintered beryllia.

12.2.VIII. *Thermal Conductivity* λ

The mean value of λ (usually measured between 20° and 100° along the lines given in VDE 0335) is generally higher than that of technical glasses and quartz glass (see Fig. B 10-43); however, it is far less than that of any metal. Except for dense high-aluminas ($\lambda = 40 - 45 \times 10^{-3}$ cal/cm-sec °C), λ normally lies between $2.8 - 8 \times 10^{-3}$. Porous ceramics naturally have lower λs than dense-sintered. At elevated temperatures, λs of silicate ceramics increase, as they do with glasses (Figs. B 12-16 and B 12-16A), and in contrast to pure oxide ceramics (Figs. B 12-65 to B 12-66).

12.2.IX. *Specific Heat* c_m

The averages, measured between 20° and 100°, lie between limits of 0.18 and 0.25 cal/g °C, and increase with temperature, as shown by the example of a type of porcelain in Fig. B 12-17.

12.2.X. *Volume Electrical Resistivity* ϱ

This parameter does not have quite such high values as that of quality technical glasses because of the ever-present impurities due to the source of the mineral raw
[12.2] materials and to techniques of manufacture of the ceramic. Figure B 10-44 gives data for glasses. However, for all dense silicate ceramics, ϱ is above $10^{11}\,\Omega$-cm. In the case of porous ceramics, the room-temperature values are obviously dependent on atmospheric moisture. The type and quantity of glassy phase in the ceramic is important in determining the value of ϱ at elevated temperatures and in fact for all the other

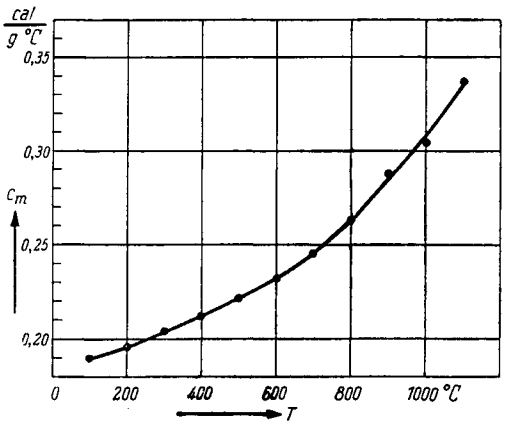


Fig. B 12-17 Average specific heat c_m (20 — T°C) of a porcelain (Berlin Porcelain) as a function of temperature T (ENDELL)

electrical properties. Since in the glassy state the alkali ion bonds are far weaker than in the crystalline state, large amounts of glassy, alkali-containing phase in a ceramic body produce, as a rule, lower values of ϱ at high temperatures, and also higher dielectric losses. To this group of ceramics belong mainly the porcelains, cordierites and ordinary steatites. In the case of certain high-fired cordierites, low-loss steatites, zircons and high-aluminas, and also forsterites, the glassy phase consists more of BaO-type glass (alkaline earth glasses), so that the electrical losses due to the glass phase are lower. Pure-crystalline, glass-free ceramics (made from pure metallic oxides) exhibit the lowest electrical losses, as compared with glassy-phase ceramics, and they also possess the highest ϱ even at elevated temperatures, generally 1 to 2 orders of magnitude greater than the corresponding silicate ceramics (Fig. B 12-67).

The predominant role of the glass phase in electrical conductivity means that at least for high temperatures the RASCH-HINRICHSEN law (10.2.X) holds for ceramics as for glasses. Therefore, the plot of $\log \varrho$ versus $1/T$ (°K) gives straight lines as for technical glasses (Figs. B 12-18 and B 12-18A; the latter figure shows these functions for some typical glasses for comparative purposes). With many ceramics, an inflexion point occurs in the $\varrho(T)$ functions somewhat below 250° (see Figs. B 12-18A and B 12-19); it

coincides roughly with the transition point determined from measurements on electrical breakdown (see 12.2.XII, especially Fig. B 12-24).

In Anglo-American countries it is usual to quote, as a figure of merit for insulation resistance the temperature at which the resistivity drops to 1 MΩ-cm, the "*Te* value", which plays a part similar to the $T_{\varkappa 100}$ point (100 MΩ-cm) of technical glasses (cf. 10.2.X). Table T 12–7 is a collection of *Te* values for typical ceramics.

The following should be said on the subject of measuring ϱ itself: while in many countries the very high resistivities of ceramics (especially at low temperatures) are usually measured by D.C. supply and galvanometer to give order-of-magnitude results (see, [12.2]

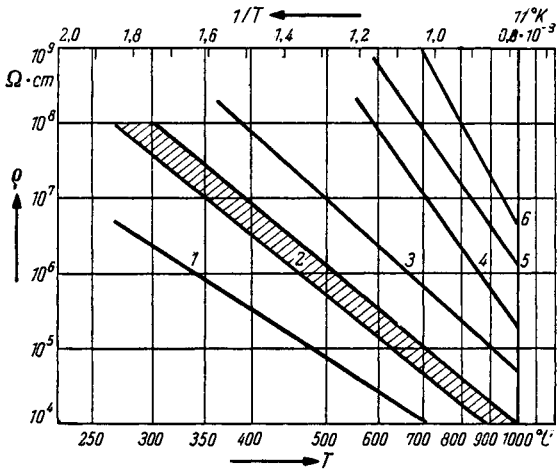


Fig. B 12-18 Electrical resistivity ϱ of some typical ceramics as temperature (T) functions, measured with A.C. (50–60 c/s)

1 hard porcelain
2 ordinary steatite
3 thermally insulating ceramic for electrical use
4 special type of steatite
} (ALBERS-SCHÖNBERG)

5 low-loss steatite
6 Forsterite
} (*THURNAUER)

e.g., CSN 124), this is not always so: according to other standards (VDE 0335), assuming that lossy test-ceramics can be replaced by a loss-free capacitor with a shunt resistor, it is recommended that the resistivity at 20° be calculated from measuring frequency f (c/s), dielectric constant ε, and loss-factor $\tan\delta$ by the expression

$$\varrho_{20} = \frac{1.8}{f \cdot \varepsilon \cdot \tan\delta}\, 10^{18}\ \Omega\text{-cm}\,.$$

The determination of ϱ at high temperatures should follow the same standards as for 50 c/s, with ordinary voltage/current measurements on flat disks 40 mm dia. and about 3 mm thick, with Pt electrodes fired solidly to the disks with platinum bright (10.4.II). See VDE Testing Spec. 0335/7.56 and VDE 0303, section 3/10.55.

Since the conductivity of glassy-phase type ceramics is due to ion mobility, as with technical glasses, and as mobility increases with T (10.2.XI), heated ceramics when

passing D.C. exhibit ion migration and hence electrolytic effects, especially the alkali ceramics (see also 12.3.I). Because of the (generally) low glass-content and the sort of applications hitherto required of fine ceramics, this effect does not play the same part in the life of a voltage or heat-stressed ceramic component as it does with glass (especially vacuum-tight glass-metal seals). In USW tubes, where ceramics are most used for

[12.2]

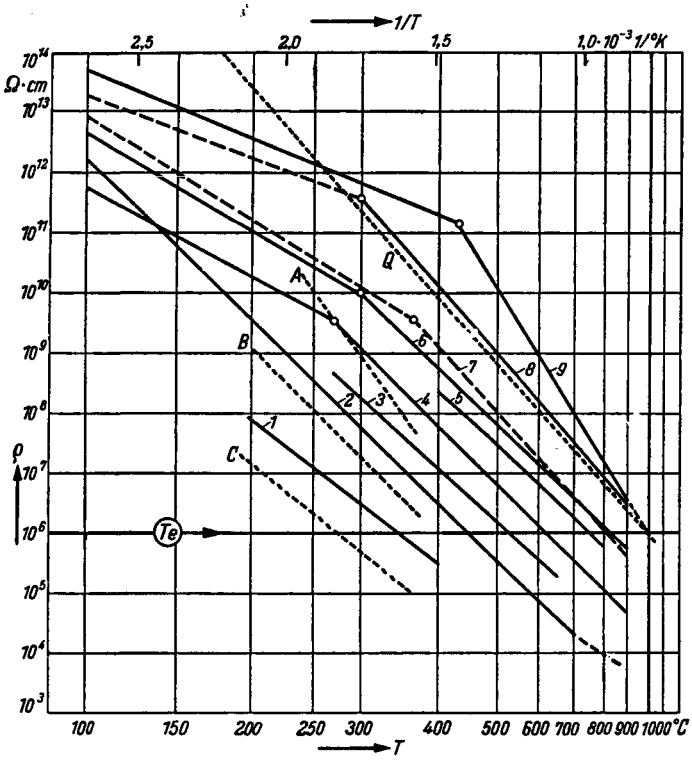


Fig. B 12-18A Electrical resistivity ϱ of some commercial ceramics as functions of temperature T

1 feldspar porcelain "Almanox 11838"; *2* ordinary steatite "Alsimag 35"; *3* zirconia mullite "Almanox 2570"; *4* natural rock Al-silicate "Lava A"; *5* high-alumina dense ceramic "Almanox 6096"; *6* high-alumina porous ceramic "Alsimag 393"; *7* rock Mg-silicate "Alsimag Lava 1136"; *8* high-alumina dense ceramic "Alsimag 614"; *9* Forsterite "Alsimag 243"

For comparison: *Q* quartz glass; *A* lead glass CORNING 0120; *B* Pyrex glass CORNING 7740; *C* soda-lime glass CORNING 0080.

Te = Te value

envelopes, one rarely encounters thermally and electrically stressed ceramic tube constructions with vacuum-tight metal lead-throughs closely spaced from each other, as in glass pinches or presses. In many fine-grain ceramics the single crystallites coalesce in the course of recrystallization and are not solely glued together by the glass phase. In such structures there is less danger of disastrous effects, i.e. inhomogeneous expansion, and fracture, should the hot glass partly electrolyze.

TABLE T 12–7. Te VALUES (TEMPERATURE AT WHICH RESISTIVITY IS 1 MΩ-cm) FOR SOME TYPICAL SILICATE CERAMICS, ARRANGED IN ASCENDING ORDER

TYPE OR TRADE NAME	Te (°C)	MFR. SEE FOOTNOTE
Fine-pore ceramic DIN Type 510–511	ca. 300	(3)
Feldspar porcelain (Almanox 11858)	349	(1)
Porcelains (DIN Type 110–120)	<400	(3)
Steatite (Alsimag 35)	440	(2)
Zircon porcelain (Stemag)	<500	(4)
Steatite, molded (DIN Type 210)	<500	(3)
Cordierite, dense (DIN Type 410)	<500	(3)
Zircon mullite (Almanox 2570)	527	(1)
Steatite, dense (DIN Type 220)	<600	(3)
Coarse-pore brown ceramic (DIN Type 512)	<600	(3)
Zirconia (Alsimag 508)	610	(2)
Soapstone, fired (Lava Grade A)	620	(2)
Steatite (Almanox 13889)	632	(1)
Zircon (Almanox 3569)	677	(1)
Fine-pore ceramic + Mg silicate (DIN Type 520)	<700	(3)
Zircon (silicate) (Alsimag 504)	700	(2)
Alumina mullite (Almanox 7873)	710	(1)
Cordierite (Almanox 5301)	743	(1)
Alumina (Almanox 6096)	749	(1)
Steatite (Alsimag 196)	750	(2)
Cordierite (Alsimag 202)	780	(2)
Alumina (Almanox 4462)	799	(1)
Fine-pore ceramic, mainly alumina (DIN Type 520)	<800	(3)
Soapstone (natural rock from Bavaria)	800	(4)
Al-silicate (Alsimag 576)	800	(2)
Natural Mg-silicate (Lava 1136)	810	(2)
Steatite (Alsimag 228)	820	(2)
Al-silicate (Alsimag 393)	835	(2)
Steatite (Alsimag 197)	840	(2)
Zircon (silicate) (Alsimag 475)	870	(2)
Al-silicate (pyrophyllite), rock from the Transvaal	600–900	–
Al-silicate (Alsimag 614)	930	(2)
Porous, machinable Steatite (DIN Type 240) e.g. Ergan	<1000	(3)
Special steatite (DIN Type 221)	<1000	(3)
Mg-silicate (Alsimag 222)	>1000	(2)
Al-silicate (Alsimag 652)	>1000	(2)
Forsterite (Alsimag 243)	>1000	(2)
(Frequenta M)	>1000	(4)

[12.2]

(1) FRENCHTOWN PORCELAIN CO. (2) AMERICAN LAVA CORP.
(3) German mfr. (4) STEMAG.

12.2.XI. *Surface Resistance* R_{ob}

This parameter lies in the range 10^{14} to $10^{17}\,\Omega$ per square if the surroundings are quite dry or the object is in vacuum. The unit Ω per square is the resistance of a square surface of any side, measured between two electrodes on opposite sides of the square see also 10.2.XII).

Inside the vacuum tube, the high degree of roughness of many types of ceramic can be very advantageous because it prevents the formation of conducting metal films from

[12.2]

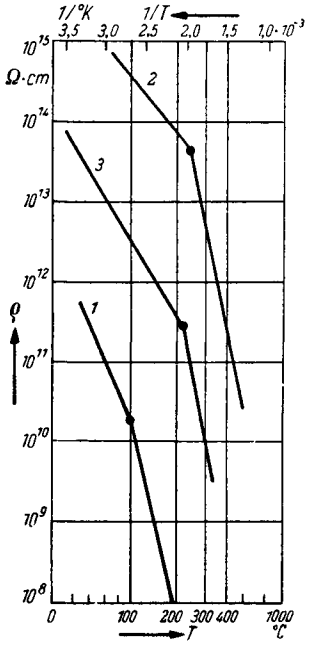


Fig. B 12-19 Electrical resistivity ϱ of various ceramics as functions of temperature T, plotted as $\log \varrho = f(1/T)$ (LINDSAY)
1 high-voltage porcelain; *2* high-alumina ceramic; *3* zirconia ceramic

stray metallic vapor, as from flash getters or overheated electrodes. For this reason, smooth components (e.g. glass pinches, see 10.4.XII, or mica support disks (see Chapter 13), are often coated with a thin layer of MgO or other such material.

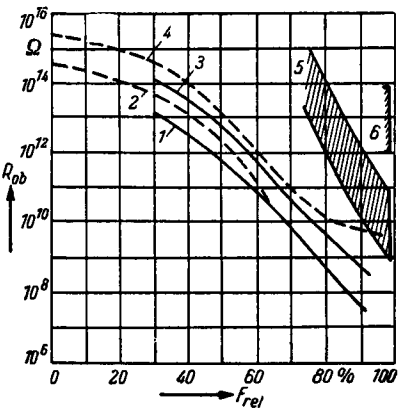
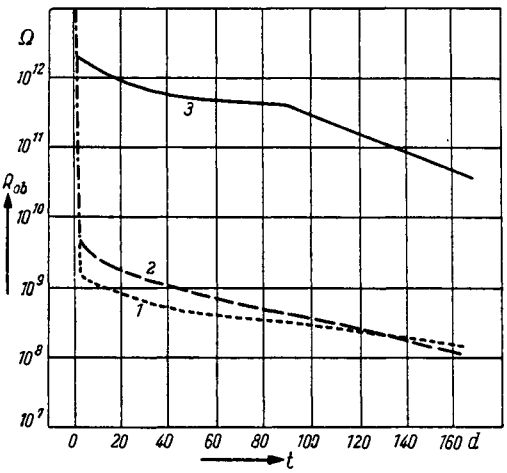


Fig. B 12-20 Surface resistance R_{ob} of porcelain and steatite as functions of relative humidity F_{rel}
1 unglazed porcelain, *2* glazed porcelain } (H. L. CURTIS, [1]ESPE)
3 unglazed porcelain, *4* glazed porcelain } (BUBLITZ)
5 steatite, untreated, limiting values
6 steatite, after application of water-repellent film, limiting values at 99% relative humidity } (ROBINSON)

The surface resistance of silicate ceramics below 100° is strongly dependent on the humidity of the surrounding atmosphere, as with glass (10.2.XII); this will therefore apply to external surfaces of ceramic envelopes or ceramic current-lead insulators like

those for tank rectifiers. Also, dust settled on the surfaces can obviously still reduce R_{ob} further. For this reason, the reduction in R_{ob} of glazed, easily cleaned ceramics is less than that of rough, unglazed. The surface resistance of ground ceramics is 1 or 2 orders of magnitude less than that of ceramics with undamaged firing skins in air saturated with water-vapor.



[12.2]

Fig. B 12-21 Effects of applying water-repellent films to ceramic surfaces: surface resistance R_{ob} of steatite ceramics, variously treated, as functions of storage time t in air at 90% relative humidity and 30°

1 unglazed untreated surface; *2* the same after wax-impregnation; *3* same after applying silicone film 5×10^{-5} cm thick

As with glass, the reduction of R_{ob} by atmospheric moisture can be effectively counteracted by applying water-repellents ("dry films"). See 10.4.XIII for a detailed account. Figures B 12-20 and B 12-21 show the influence of such treatment.

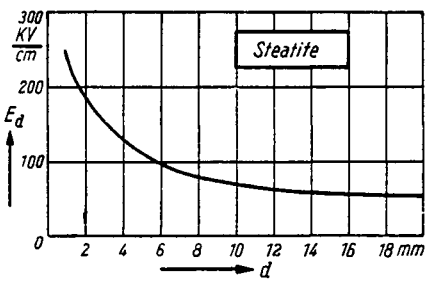


Fig. B 12-22 Electrical breakdown strength E_d of steatite ceramics as a function of thickness d of test-piece (AMERICAN LAVA CORP., Chattanooga, Tenn., USA)

Measurement of R_{ob} is generally carried out in tropical-testing equipment (air-conditioned chambers) between two graphite or noble-metal strips (100 mm long, 10 ± 1 mm apart), with 1 kV D.C. and a galvanometer; current is measured 1 min after application of voltage (see also VDE 0335 and 0303). The Ω per square value is calculated from the ohmic value of the 10×100 mm² surface by multiplying by 10.

12.2.XII. *Electrical Breakdown Strength* E_d

The same principles apply here as to glass (10.2.XIV). In particular, the value of E_d depends on the following factors: duration of stress, voltage rise-rate, frequency, wave-

form, field distribution, and above all the thickness of the test-piece (Fig. B 12-22). Test conditions are therefore standardized to ensure an unambiguous result (see, e.g., ASTM, BSI, ČSN, VDE).

[12.2]

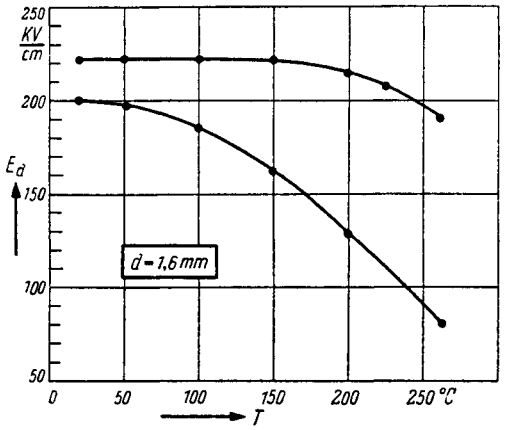


Fig. B 12-23 Electrical breakdown strength E_d of two steatites, 1.6 mm thick, as functions of temperature T

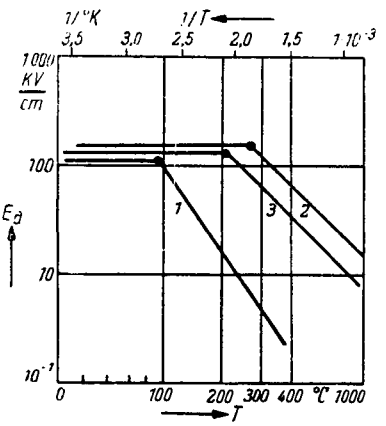


Fig. B 12-24 Electrical breakdown strength E_d of some ceramics, as functions of temperature T (LINDSAY). ● = transition point

1 high-voltage porcelain; *2* high-alumina ceramic; *3* zirconia ceramic

E_d for dense-fired ceramics can reach 5–10 times that of air. This parameter (as shown in Fig. B 12-23) is fairly temperature-independent up to the so-called "transition point" (the range of ionization breakdown), but it then falls rapidly (thermal breakdown

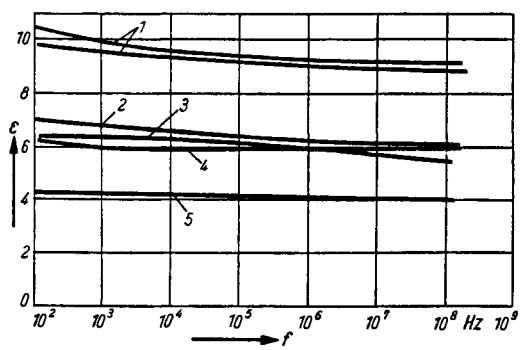


Fig. B 12-25 Dielectric constants ε of different types of ceramic, at room temperature, as functions of frequency f ([1]RUSSELL) (see also Table T 12-12)

1 zirconia porcelains; *2* ordinary steatite; *3* high-voltage porcelain; *4* special steatite; *5* (for comparison) fused silica

range). This discontinuity is particularly marked in many ceramics if one plots E_d logarithmically against $1/T$ (°K) (see Fig. B 12-24), and it shows up also in corresponding inflexions in the plots of $\log \varrho$ vs. $1/T$ (see Fig. B 12-19) and $\log(\tan\delta)$ vs. $1/T$ (see Fig. B 12-30).

12.2.XIII. *Dielectric Constant ε and Loss Angle tan δ*

ε-values of dense ceramics (if rutile and barium titanate capacitor-ceramics are excepted) are of the same order of magnitude as those of the other electrical insulators, but in general are somewhat higher than those of technical glasses. Porous ceramics naturally have lower ε-values (4.5–5) than dense-fired (5–6) as shown in Fig. B 12-25 and Table T 12–12. For all ordinary ceramics, ε rises with T, again with the exception of some capacitor ceramics not treated here, as shown by Fig. B 12-26; however, the rise is less the higher the frequency of measurement (Fig. B 12-27) and for 10^{10} c/s up to 500° is quite small (Figs. B 12-27, B 12-28). [12.2]

Tanδ, by and large, is much less than for technical glasses especially at high frequencies; this is clearly shown by comparing Fig. B 12-29 with Fig. B 10-73 and the corre-

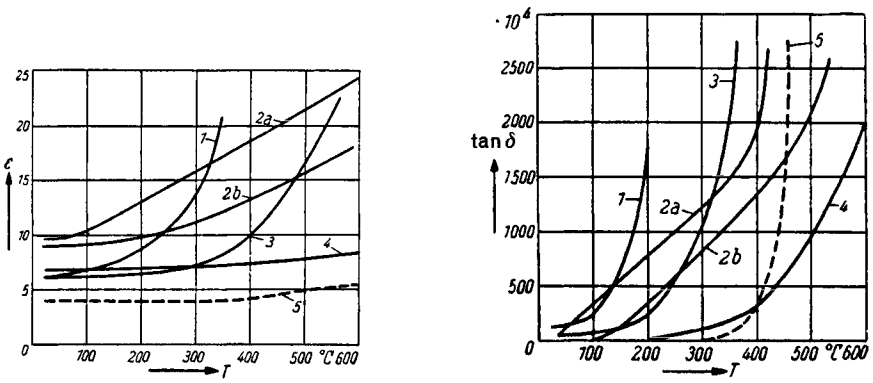


Fig. B 12-26 Dielectric constants ε and loss angles tanδ of some ceramics measured at 10^5 c/s, as functions of temperature T ([1]RUSSELL)

1 high-voltage porcelain; *2a* zirconia porcelain; *2b* special zirconia porcelain; *3* ordinary steatite; *4* specia steatite; *5* (for comparison) fused silica

sponding tabulated values for commercial ceramics (Table T 12–12) with those for commercial glasses (Table T 10–4, especially A 1). As frequency rises, tan δ falls up to 10^6 to 10^8 c/s, and then increases again somewhat only at very high frequency (Table T 12–12 and Fig. B 12-29).

For all ceramics tan δ increases with T, the less so the higher the frequency (Figs. B 12-27, and B 12-29A). If tanδ is plotted on log scale against $1/T$ (°K) on a linear scale, transition points are noticeable with many ceramics, mentioned earlier in connexion with electrical breakdown and resistivity (Figs. B 12-24, B 12-19 respectively). Above this point, tanδ rises extremely rapidly (Fig. B 12-30). Since tan δ is not the sole determinant of dielectric loss, but rather ε · tanδ (so-called "dielectric loss factor", see 10.2.XIII), Fig. B 12-31 shows this coefficient as a function of T for some ceramics in comparison with a low-loss glass; naturally, the factor rises with T, being essentially determined by tan δ. Finally, Fig. B 12-32 gives this factor for some commercial ceramics as a frequency function, in comparison with fused silica and two glasses of value in electrical applications in vacuum tube construction. This comparison shows clearly the superiority of certain ceramics in the UHF range. As can be seen, steatite 228 and 196

(curves *5* and *7*) are not so lossy as Pb-glass (curve *10*); the well-known low-loss glass CORNING 7070 (curves *1–9*) is a lower loss material than the steatites mentioned, but is inferior to porous alumina ceramic (curve *8*), and above all to forsterite (curves *3* and *6*). The extremely low loss properties of pure fused silica (curve *2*) in the UHF range above 10^8 c/s are not attained even by the best ceramics so far made.

[12.2]

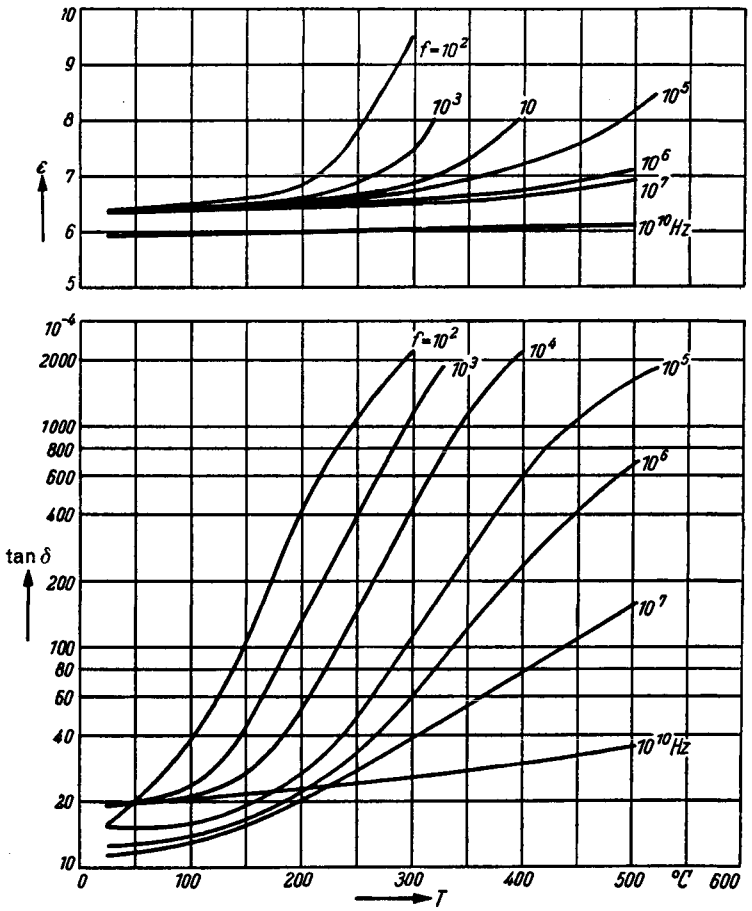
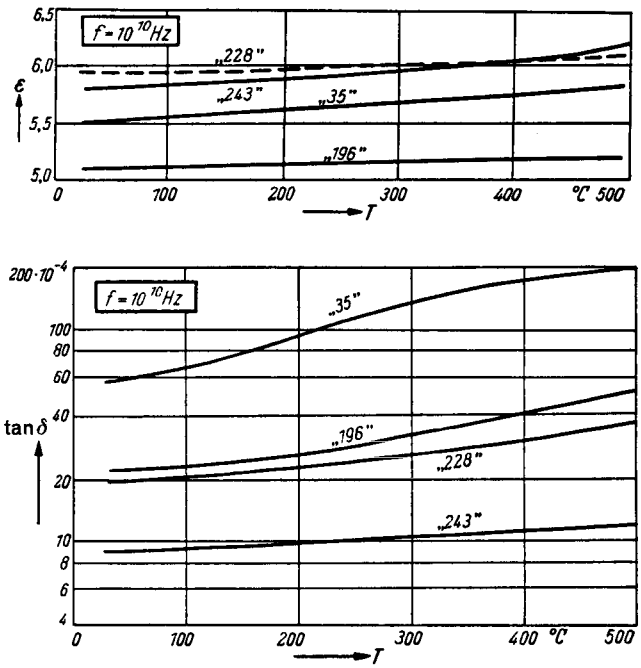


Fig. B 12-27 Dielectric constants ε and loss angles $\tan\delta$ of a low-loss steatite (Alsimag 228) as functions of temperature T, for various frequencies f (HIPPEL)

ε and $\tan\delta$ are determined as functions of frequency and temperature by means of fired-on Ag or Pt electrodes, and the normal measuring equipment (see, e.g., VDE 0335/7.56, para 22, and VDE 0303, part 4/10.55, para 4).

The UHF loss ($\varepsilon \cdot \tan\delta$) of a ceramic can be monitored relatively simply by comparing with a standard material; a test-piece (e.g. a disk) is locally coated with a color-conversion temperature indicator (see 10.5) and then introduced into a strong H.F. field



[12.2]

Fig. B 12-28 Dielectric constants ε and loss angles $\tan\delta$ of some commercial ceramics at 10^{10} c/s, as functions of temperature T (HIPPEL)

Alsimag 35: ordinary steatite
Alsimag 196: low-loss steatite
Alsimag 228: special steatite
Alsimag 243: Forsterite
} see Table T 12–12

TABLE T 12–8. LOSS ANGLE TAN δ (MEASURED AT 10^6 c/s, ROOM TEMPERATURE) OF THE CHIEF TYPES OF CERAMIC, ARRANGED IN DESCENDING ORDER

CERAMIC TYPE	TAN δ (10^{-4})
Lava A (natural rock) (Al-silicate)	100
Hard porcelain DIN Type 110	60–120
Cordierite, porous (water take-up = 8.5%)	40–82
Cordierite, dense, type DIN 410	40–70
Zircon mullite	32
Steatite, dense, DIN Type 220	15–20
Steatite Alsimag	12–35
Zircon	8–17
Forsterite (Alsimag 243)	4
High-aluminas (Alsimag)	3–7
Special Steatite DIN Type 221	3–5
Soapstone, Lava 1136 (Mg-silicate)	3
Mg-silicate, porous (Alsimag 222)	2–4

of the frequency in question. Measurement is made of the time needed for the indicator dye to alter, and this is compared with the corresponding time for a test-piece made from the standard material, under the same conditions.

H.F. ceramics are classified in the USA by their loss factor (Table T 12–9). The class to which a ceramic belongs is determined only after 48 hr immersion in distilled water followed by quick drying with a cloth.

[12.2]

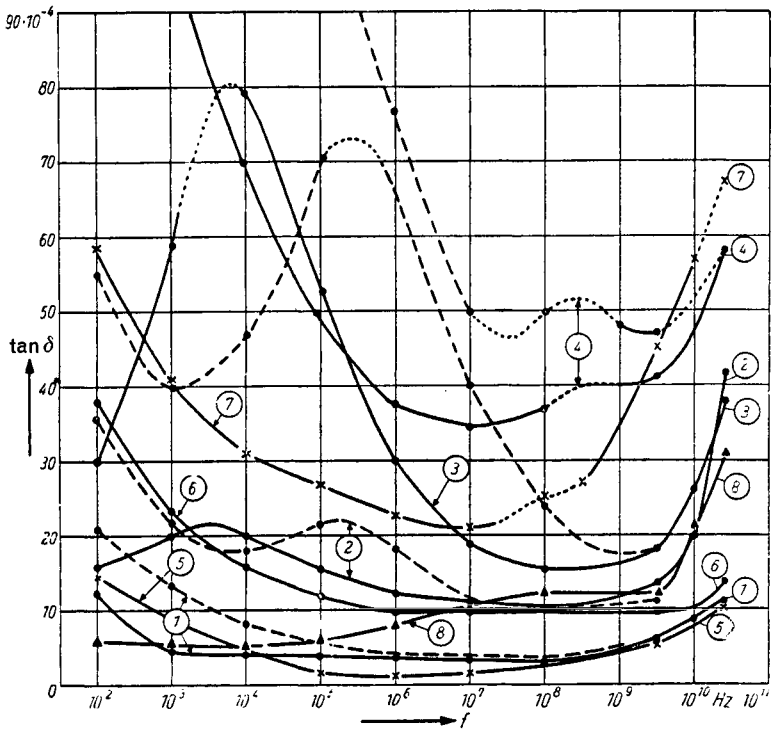


Fig. B 12-29 Dielectric loss angle tanδ of various ceramics at room temperature, as functions of frequency f

Curve *8* is added for comparison: it relates to a very low-loss glass (CORNING 7070)

——— 23–25°; - - - - interpolated

CURVE NO.	CERAMIC
1	Forsterite, Alsimag 243
2	Steatite, Alsimag 228
3	Steatite, Alsimag 196
4	Steatite, Alsimag 35
5	Bell Ceramic F-66
6	Alumina, Alsimag 393
7	Zr ceramic, Coors Zi-4
8	CORNING 7070 (comparison)

12.2.XIV. *Optical Transparency of Silicate Ceramics*

Thin, dense-fired, colorless ceramics transmit some light and heat; ordinary porcelain 1.5 mm thick transmits about 5% of incident light. High-fired ceramics are not, however, transparent. This is because the glassy phase contains crystallites (e.g.quartz and mullite crystals in porcelain) which act as dispersion centers for any light or heat radiation of wavelength equal to or less than crystal diameter. From this it will be clear that with

TABLE T 12-9. DIELECTRIC-LOSS CLASSIFICATION FOR CERAMICS (USA JOINT ARMY AND NAVY SPECIFICATION JAN-I-10)

GRADE	MAX. PERMISSIBLE LOSS FACTOR $\varepsilon \cdot \tan\delta$ (1)	EXAMPLES
L-1	0.1500	—
L-2	0.0700	Feldspar porcelain Almanox 11858
L-3	0.0350	Steatite Alsimag 35
L-4	0.0160	Steatite Alsimag 13889 Steatite Alsimag 196 Unglazed Alsimag 228
L-5	0.0080	Glazed Steatite Alsimag 228 Unglazed Forsterite Alsimag 243
L-6	0.0040	Glazed Forsterite Alsimag 243

(1) $\varepsilon < 12$.

[12.2]

porcelain the transmission is higher the lower the mullite content and the more the quartz particles in the batch are dissolved in firing, i.e. the higher the glass-phase content.

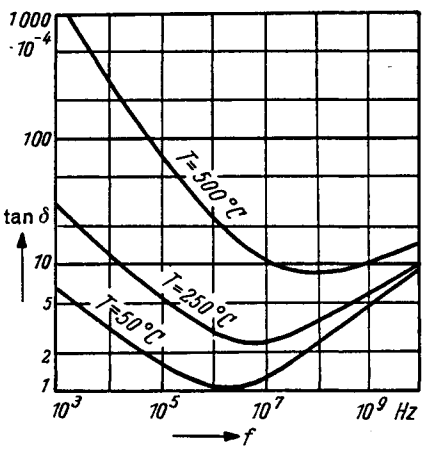


Fig. B 12-29A Dielectric loss angle $\tan\delta$ of a low-loss steatite ceramic, as a function of frequency f for different temperatures T (2RIGTERINK)

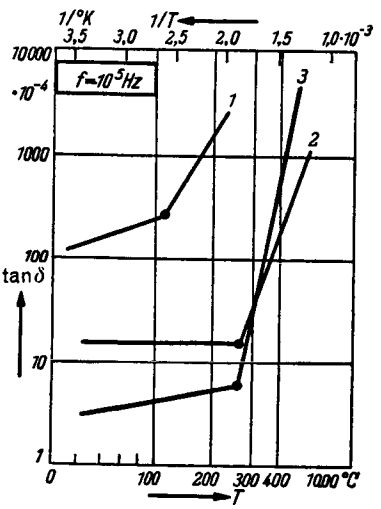


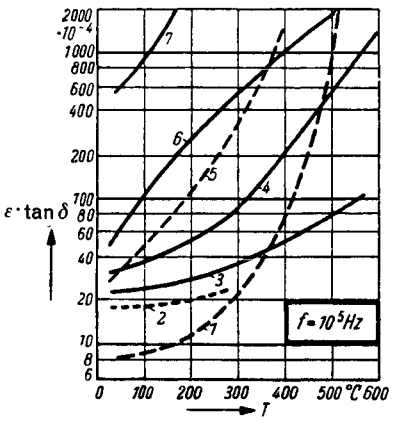
Fig. B 12-30 Loss angle $\tan\delta$ of some ceramics and quartz measured at 10^5 c/s and plotted logarithmically against reciprocal temperature (°K) (LINDSAY)

Knees of curves = transition points (cf. also Figs. B 12-19 and B 12-24)

1 high-voltage porcelain; *2* high-alumina ceramic; *3* quartz glass

This can be demonstrated in the laboratory by tests with precipitated silica (instead of quartz), which is completely dissolved on firing; the porcelain shard in this case attains the maximum overall transparency for the given composition (2DIETZEL).

Because of crystallites, a ceramic body of reasonable thickness scarcely transmits even thermal radiation; radiative dissipation of heat from hot electrodes in thick-walled ceramic electron tubes is no greater than with glass or quartz and they must be cooled by conduction. This can occur partly through metallic electrode leads of adequate dimensions, partly by conduction of energy absorbed in the ceramic walls through these and removal of this energy from the outer surface of the ceramic tube by means of a coolant (convected or forced-draught air, liquid, etc.). Walls of ceramic vacuum tubes run hotter than glass, as do metal walls, for the same power dissipation and surface [12.2] area of wall.



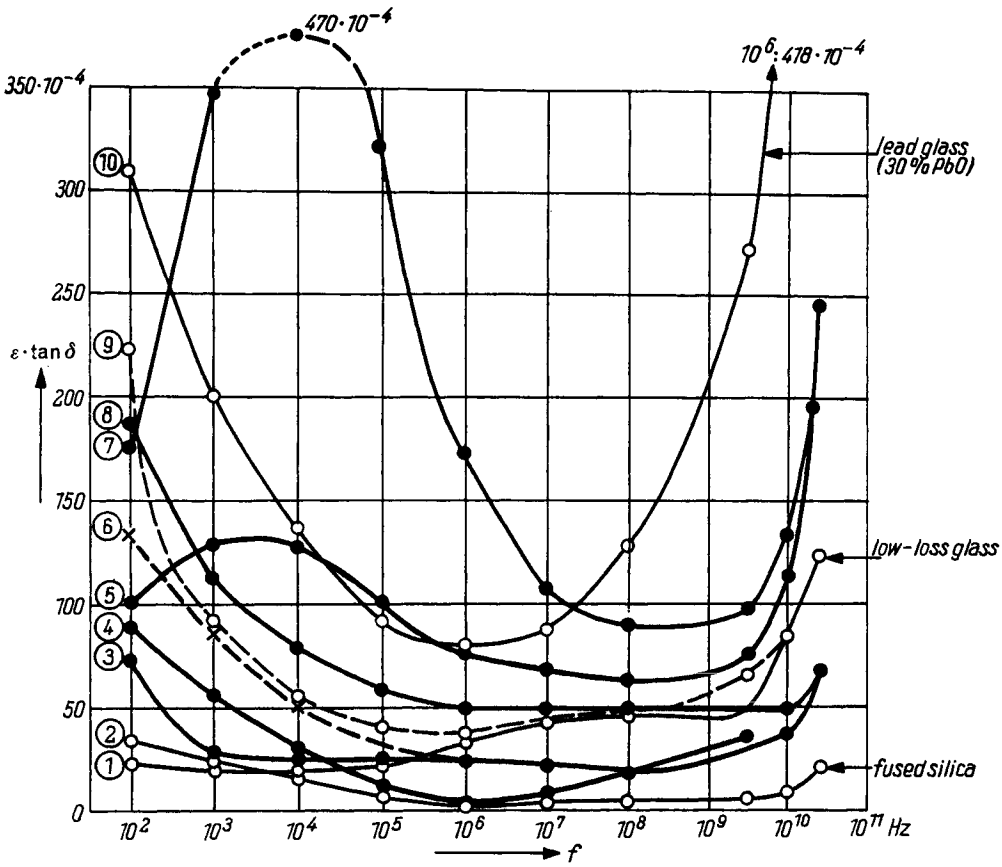
CERAMIC	CURVE NO.	CERAMIC	CURVE NO.
Hard porcelain	7	Zr porcelain	6
H.F. steatite (Frequenta)	4	CORNING 7070 glass	5
Forsterite	3	Quartz glass	1
		Muscovite mica	2

Fig. B 12-31 Dielectric loss factor $\varepsilon \cdot \tan\delta$ of various materials at 10^5 c/s as functions of temperature T, in comparison with mica, quartz glass and a particularly low-loss borosilicate glass (data collected by STEYSKAL)

Obviously, the well-known optical strain-measuring processes using polarized light (10.3.IX) are not applicable to ceramics because of their opacity. However, the ceramic will transmit electromagnetic radiation of wavelength much greater than the diameter of dispersion centers, and if such radiation rather than light is employed, qualitative and quantitative measurements of strain and of texture can be made. For further details see DIETZEL, GOLDHAMMER.

12.2.XV. *Vacuum Tightness*

Silicate ceramics can be sintered at temperatures relatively low compared with pure oxide ceramics, and so far as experimental results exist, they show that vacuum-tightness of these ceramics and possibly also of bonds between them and fired-on metal layers (Chapter 32) depends on one overriding factor: the presence of even a small amount of glassy phase (Table T 12–14). This phase either fills the pores always present in the ceramic, or at least closes them off on all sides and so prevents interconnexions between them. The most extensive possible removal of the air content of the starting batch is essential for making vacuum-tight ceramics; it is preferable to pump the batch when moist and plastic, at about 20 Torr (see Figs. B 12-2, B 12-2A, B 12-3B); or, if the envelope is being cast, the slip should be deaerated by at least 1 hr intensive stirring under reduced pressure. Vacuum-tightness of an ordinary silicate ceramic like porcelain will obviously be much increased (Fig. B 12-35E) by applying a durable refractory glaze



[12.2]

Fig. B 12-32 Dielectric loss factor $\varepsilon \cdot \tan\delta$ of various H.F. ceramics as functions of frequency f, compared with quartz glass and two technical glasses

Ceramics: 25° 85°

Glasses: 25° 100°

CERAMIC	T °C	CURVE NO.
Forsterite Alsimag 243	22	3
	85	6
Bell F 66	25	4
Porous Al_2O_3 Alsimag 393	25	8
Special steatite Alsimag 228	25	5
Ordinary steatite Alsimag 196	25	7
For comparison:		
Quartz glass (fused silica)	25	2
Low-loss glass CORNING 7070	23	1
	100	9
Lead glass CORNING 0120	23	10

(SK no. 10–14, 1300–1410°) that resists atmospheric corrosion—provided this is permitted by the design. Experience shows that steatite (12.3.III*a*) will make vacuum-tight mass-produced envelopes if 1.8 mm thick or more, even when unglazed (PULFRICH). With forsterites one can achieve the same result with walls down to 0.5 mm ([2]NAVIAS).

MONTGAILLARD carried out permeability measurements on vacuum tubes made of 10 cm^2 of metal and 7.5 of ceramic (with 95% Al_2O_3) with brazed seams: at 25° the H_2 permeability was 8×10^{-7} liters (10^{-3} Torr, 20°)/sec/cm^2 surface, and at 500° the figure was 1.5×10^{-3}. The gauge pressure of H_2 was apparently 1 atm. No wall-thickness data for metal or ceramic were provided, however.

Similarly, BECKER observed rapid penetration of H_2 through tube walls above 200°, using a mass-spectrometer. However, it was not made clear whether H_2 penetrated the ceramic part of the wall, the metal part (Kovar) also present, or the brazing.

[12.2]

12.2.XVI. *Gas Released from Silicate Ceramics*

Many silicate ceramics can be viewed in the same way as technical glasses (10.5) because their glass-phase content is high. Mass-spectrometer investigations of the gas from silicate ceramic AI 200 of the COORS PORCELAIN Co. at temperatures below 1000°

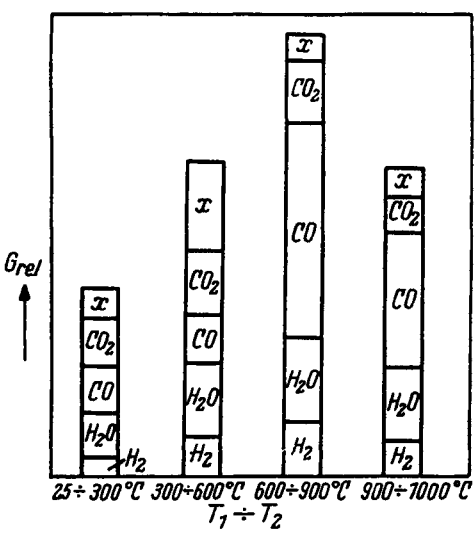


Fig. B 12-32A. Relative amounts of gas released G_{rel} from a Forsterite ceramic for vacuum tube envelopes; used amounts are shown for various ranges of temperature $T_1 \div T_2$, and are divided by type of gas as determined mass-spectroscopically (GRIESSEL) (x = other gases)

revealed remarkable freedom from gas, but above 1000° detectable amounts of CO were given off, although ThW cathodes in Zr-gettered tubes were not poisoned up to the softening point of the ceramic (P. D. WILLIAMS).

See Fig. B 12-32A for relative degassing of a Forsterite ceramic.

In degassing ceramics it should be further noted that traces of Fe_2O_3 (dissociation pressure *ca.* 10^{-6} Torr at 800°) constitute a particularly prolonged source of O_2 at elevated degassing temperatures; this effect is often so pronounced that it is mistaken for a leak-hole or genuine permeability to O_2 (F. J. NORTON).

12.2.XVII. *Chemical Properties of Silicate Ceramics*

These obviously depend on the detailed composition of the ceramic; in general, dense ceramics are more inert than porous ones. Technical silicates are resistant to atmosphere even in the presence of gases, vapors or deposits containing salts, acids or alkalis, with the exception of vapors containing HF. This is the cause of their resistance to weathering, "sneak" (surface leakage) currents and arc-over. When in direct contact with liquid acids, many ceramics resist decomposition to gas-phase silicon fluoride; again with the exception of HF acid. Acid-proof porcelain, for example, when boiled in HCl should not lose more than 0.7 mg/dm^2 of exposed surface, in 2 N soda solution not more than 21 mg/dm^2. Silicate ceramics are attacked by fused alkalis and alkali carbonates, especially at elevated temperatures, in accordance with their silicate content; however, they are less affected than glass. [12.3]

12.3. Special Commercial Silicate Ceramics; their Properties and Applications in Vacuum Technology

Only the "fine ceramics" out of the large number of possible and commercially available silicate ceramics can be treated within the scope of this book. Of these, only those that are or could be used in making components for tubes or discharge devices are discussed: porcelains, naturally-occurring rock material, steatites, forsterites, cordierites, aluminosilicates, Zr-ceramics and alkaline earth porcelains.

The discovery of new sources of mineral raw materials, technically better or politically more convenient, and partly also questions of patent right, are often the cause of new fine ceramics appearing on the market, without it always being clear whether compelling *technical* needs have justified their appearance. Reliable assignment of a commercial ceramic to a known grouping is often made difficult by the number of initial materials and by efforts on the part of the manufacturer to keep secret the exact composition of the ceramic and new materials, and also the manufacturing process. From what has been said before, it will be clear that secrecy on the subject of manufacture can be preserved much more successfully here than by the glass industry, where chemical analysis of a commercial glass usually gives a fairly good indication of how it was made. A systematic standard collection of fine ceramics exists therefore only in DIN Norm 40685/1.57 (latest version 1957), treated only from the standpoint of electrical insulation.

These considerations, plus the divergent interests of the ceramic industry and the vacuum tube industry with its exacting requirements and relatively small orders, has led stage by stage to a point where the tube manufacturer has begun to make his own ceramics. Examples of this are TELEFUNKEN 1940 (see HUNT), GENERAL ELECTRIC (see [2]NAVIAS), SYLVANIA (see STANISLAW). However, in general, ceramic parts for tube manufacture—mostly fully finished in all dimensional details—are drawn from the ceramic manufacturer, with the exception of some easily worked materials for modeling or patterns like soapstone (12.3.II) or Ergan (12.3.III*b*).

[12.3]

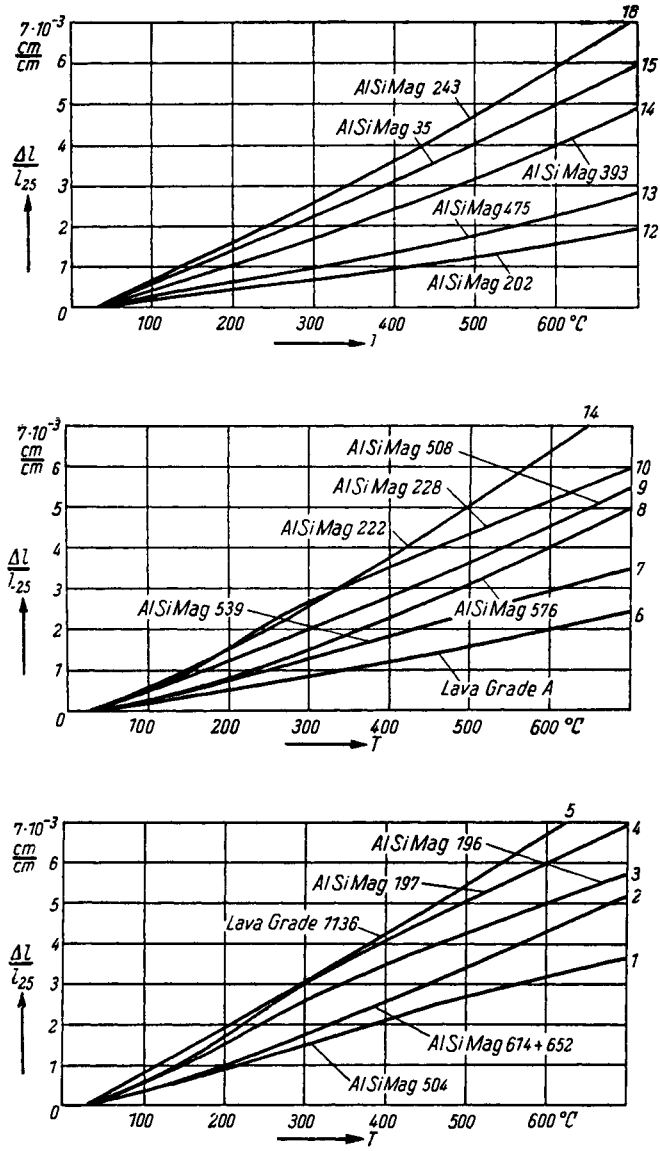


Fig. B 12-33 Thermal expansion characteristics of American fine-grain ceramics (made by AMERICAN LAVA CORP., Chattanooga, Tenn., USA)

TYPE	CURVE	TYPE	CURVE	TYPE	CURVE
Alsimag 35	15	Alsimag 243	16	Alsimag 576	8
Alsimag 196	3	Alsimag 393	14	Alsimag 614	2
Alsimag 197	4	Alsimag 475	13	Alsimag 652	2
Alsimag 202	12	Alsimag 504	1	Lava 1136	5
Alsimag 222	11	Alsimag 508	9	Lava A	6
Alsimag 228	10	Alsimag 539 (SiC)	7		

Table T 12–10 gives a survey of the compositions and applications of commercial ceramics that have been published. Table T 12–11 contains the chief properties of commercial ceramics taken from manufacturers' data or specifications. The latter table is supplemented by Table T 12–12 for ε and $\tan\delta$ and a series of graphs especially Figs. B 12-33 and B 12-34, referred to in the appropriate columns of the table.

[12.3]

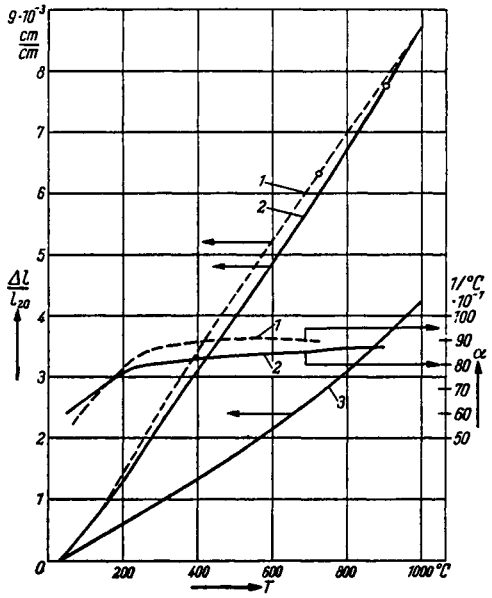


Fig. B 12-34 Relative thermal expansion $\Delta l/l_{20}$ and coefficient α of Calit (*1*), Frequenta (2), and Berlin Porcelain (*3*), as functions of temperature T

TABLE T 12–10. COMPOSITION AND APPLICATIONS OF COMMERCIAL CERAMICS, ARRANGED BY MFR.

A: American ceramics

A 1: Mfr. AMER. LAVA CORP. (their data)

NO.	TRADE NAME	CONSISTS MAINLY OF	STRUCTURE AND COLOR	CHARACTERISTICS	CHIEF USES
1	Alsimag 35	Steatite, clinoenstatite	Dense, white	Strong, good electrical properties, (L–3)[1]	Quality insulators
2	Alsimag 178	Cordierite	Porous, white	Like Alsimag 202	
3	Alsimag 196	Steatite, clinoenstatite	Dense, white	Low loss (better than Alsimag 35),strong, precise dimensions (L–1)[1]	R.F.
4	Alsimag 197	As Alsimag 196	Dense, white	High resistance at elevated temps.	Heater-wire supports
5	Alsimag 202	Cordierite	Porous, yellow-brown	Low α, high thermal shock resistance	Insulators for heaters and thermocouples
6	Alsimag 206	Clinoenstatite	Dense, gray	As Alsimag 35	
7	Alsimag 207	As No. 6	Dense, brown	As Alsimag 35	
8	Alsimag 209	As No. 6	Dense, gray	As Alsimag 197	
9	Alsimag 210	As No. 6	Dense, brown	As Alsimag 197	
10	Alsimag 211S	Steatite	Dense	Absorbs no gas. Strong. Suitable for mass-production	Insulators inside tubes

11	Alsimag 222	Mg-silicate	Highly porous	Machinable in the fired state	Pattern-making and repairing
12	Alsimag 228	Steatite, clinoenstatite	Dense, white	Exceptional strength, low loss	H.F. equipment
13	Alsimag 243	Forsterite	Dense, red-yellow	Very low loss (I.–5)[1], close tolerances by grinding, α (20—300 °C) $\approx 100 \times 10^{-7}$/°C	Vacuum-tight ceramic-metal seals
14	Alsimag 393	Al_2O_3 (93%), SiO_2 (6%), MgO (1%)	Very porous	Easily degassed, good elec. resistance at high temps.	Internal insulators for vacuum tubes
15	Alsimag 475	$ZrO_2 \cdot SiO_2$	Dense, white	Strong, high thermal shock resistance, (L–4)[1]	
16	Alsimag 504	As No. 15	Very porous	High thermal shock resistance	Heating plates
17	Alsimag 508	ZrO_2	Very porous	High T_{soft} (2400 °C)	High temp. applications, simple shapes only
18	Alsimag 513	Al_2O_3 (85%)	Dense, pink	As Alsimag 576	
19	Alsimag 544	Al_2O_3 (93%)	Porous	Easily degassed, good elec. resistance	As 393, but stronger
20	Alsimag 547	Cordierite, brown	Semiporous, brown	As Alsimag 202	
21	Alsimag 548	Very pure Al_2O_3	Very porous	$T_{soft} = 2050$ °C	Insulators for D.H. oxide cathodes
22	Alsimag 576	Al_2O_3 (85%)	Dense, white	Most expensive alumina, very strong	Large components for vacuum-tight, brazed lead-ins
23	Alsimag 614	Al_2O_3 (96%)	Dense, white	Very strong, low loss, $T_{soft} = 1650$ °C	Specially high-strength parts with low losses and high thermal conductivity
24	Alsimag 652	Al_2O_3 (98%)	Dense, white	Extremely strong, low loss, $T_{soft} = 1700$ °C	

[1] See Table T 12–9.

TABLE T 12–10 *(continued)*

NO.	TRADE NAME	CONSISTS MAINLY OF	STRUCTURE AND COLOR	CHARACTERISTICS	CHIEF USES
25	Lava Grade A	Natural Al-silicate (Pyrophyllite), fired in reducing atmosphere	Slightly porous, pink	High thermal shock resistance	Large piece-parts of precise dimensions
26	Lava 1136	Natural soapstone (Mg-	Slightly	Excellent elec. properties, small	Internal insulating parts of small
27	Lava 1137	silicate), fired as No. 25	porous, yellow-brown	tolerances, easy to degas	vacuum tubes
A 4 Mfr.: FRENCHTOWN PORCELAIN CO. (their data)					
1	Almanox 2570	Zr-mullite	Dense, white	Low α, high elec. breakdown strength	Cheap all-purpose material, lower losses than porcelain
2	Almanox 3569	Zircon, $ZrO_2 \cdot SiO_2$	Dense, white	Like 2570, but better elec. properties at high temps.	
3	Almanox 4462	Al_2O_3, alumina	Dense, brown	Very high thermal conductivity, strong	
4	Almanox 5301	Cordierite	Porous, reddish-yellow	Very low α, high thermal shock resistance	Thermal insulators subject to sharp temp. variation
5	Almanox 6096	Alumina, Al_2O_3	Dense, white	Like 4462 but not so good values	
6	Almanox 7873	Alumina-mullite	Dense, white	Relatively high thermal conductivity strength	Complex parts
7	Almanox 11858	Feldspar porcelain	Dense, white	Good mechanical strength and elec. properties	H.V. porcelain
8	Almanox 13889	Steatite	Dense, gray	L–4 Steatite	Parts in H.F. fields

D: German standardized ceramics (from DIN-Norm, partly amplified). Mfr.: see Table T 12–11, Dα

DIN TYPE	DESCRIPTION	TYPICAL STARTING MATERIALS AND COMPOSITION (%)	STRUCTURE	POSSIBLE WAYS OF FORMING[1]	CHARACTERISTICS	USED MAINLY FOR
110	Hard porcelain	Quartz, kaolin, and feldspar	Dense	G, D, S, W	Good mechanical and elec., thermally serviceable	High or low voltage insulators, and large L.V. insulators
111	(High-fired porcelain)	75SiO_2, 22Al_2O_3, 3K_2O (Na_2O)	Dense	P		Large L.V. insulators
120	Fine stoneware	Stoneware, schist 55SiO_2, 24Al_2O_3, 14Fe_2O_3, 3K_2O(Na_2O), 4MgO(CaO)	Dense	P, W	As above	As above
210	Low-fired steatite-types	Talc with serpentine, kaolin (60SiO_2, 5Al_2O_3, 24MgO, 4Fe_2O_3, 6CaO, 1K_2O)	Dense	P	Mechanically very good, elec. good	As above
220	Ordinary steatites	Soapstone, kaolin, feldspar (64SiO_2, 7Al_2O_3, 26MgO, 1.5Fe_2O_3, 1.5K_2O)	Dense	G, D, S, P, W	As above, tan δ low also	H.V. and L.V. insulators, esp. for H.F., electrothermal components
221	Special steatites	Soapstone, kaolin, Ba-carbonate (58SiO_2, 6Al_2O_3, 27MgO, 8BaO, 1Fe_2O_3)	Dense	as above	Very strong, elec. good, low tan δ	
240	Porous Mg-silicates	e.g. Ergan: 14 clay, 8 talc, 78Mg-orthosilicate (44SiO_2, 9Al_2O_3, 47MgO)	Porous	S, P	Can be worked after firing, small tan δ	Modeled parts, internal insulators for vacuum tubes
310—351 are capacitor materials, not treated here						
410	Dense cordierite	Kaolin, soapstone, possibly magnesite, and also quartz, feldspar (60SiO_2, 24Al_2O_3, 11MgO, 4Fe_2O_3, 1 CaO(Na_2O))	Dense	G, D, S, P, W	Very low α, high thermal shock resistance	Thermal shock resistant insulators
510	Porous products clay-Mg-hydrosilicates	Varying amounts of SiO_2, Al_2O_3, MgO, Fe_2O_3, (CaO), Na_2O or K_2O	Fine-pore, white	G, D, S, P, W	High thermal shock resistance	Arc killers, supports for alloy heater material inert to 1000 °C
511			Fine-pore, dark			
512			Coarse-pore, brown			

[1] G = cast; D = turned; S = extruded; P = molded; W = white-worked (machined after drying or after first bake).

TABLE T 12–10 *(continued)*

D: German standardized ceramics. Mfr.: see Table T 12–11, Dα *(continued)*

DIN TYPE	DESCRIPTION		TYPICAL STARTING MATERIALS AND COMPOSITION (%)		STRUCTURE	POSSIBLE WAYS OF FORMING[1]	CHARACTERISTICS	USED MAINLY FOR
520	Porous products	Cordierite	As above but Mg-silicate > 20%	Soapstone or talc addition	Finepore, white to brown	G, D, S, P, W	High thermal shock resistance, very small α	As above, but inert up to 1200 °C
530		Alumina	As 510, but mostly Al_2O_3	Al_2O_3 added	As above	G, D, S, P, W	High thermal shock resistance	As above but inert to above 1300 °C
	Dense high-alumina bodies	Sillimanite bodies	Kaolin, corundum, feldspar and sillimanite (50—65 Al_2O_3, rest SiO_2, CaO, MgO, Na_2O, K_2O)		Dense	G, D, S, P, W	Mechanically good, high λ[2], very refractory	Pyrometer tubes H.T. insulators
610		Mullite bodies	Kaolin corundum, feldspar (70—75 Al_2O_3, rest SiO_2, MgO, CaO)		Dense	G, D, S, P, W	Mechanically good, high λ[2], very refractory	H.T. insulators
		Corundum bodies	Corundum, kaolin, alkali earths (86 Al_2O_3, 11 SiO_2, 3CaO, [MgO])		Dense	G, D, S, P, W	As above	H.V. envelopes sparkplugs
710	Oxide ceramics	Alumina	Almost pure Al_2O_3		Dense-sintered	G, D, S, P, W	Mechanically very good, very hard, λ[2] very high, ϱ[3] very high	Insulating parts for vacuum tubes and
720		Magnesia	Almost pure MgO		Porous-sintered	G, D, S, P, W	Mechanically good, hard, λ[2] medium high, ϱ[3] very high	H.T. furnaces (very refractory)
730		Stabilized zirconia	ZrO_2 + additives		Dense-sintered	G, D, S, P, W	Mechanically very good, very hard, λ[2] low, ϱ[3] very high	(710 also for sparkplugs)

(1) G = cast; D = turned; S = extruded; P = molded; W = white-worked (machined after drying or after first bake).
(2) λ = thermal conductivity at 20 °C.
(3) ϱ = electrical resistivity at ordinary temperatures.

S: Swiss ceramics

S 1 Mfr.: SCHWEIZER ISOLA WERKE, Breitenbach-SO (data from WOLF)

NO.	TRADE NAME	COMPOSED MAINLY OF	STRUCTURE	CHARACTERISTICS	MAINLY USED FOR
1	Alphastea	Forsterite	Dense	High α[1]	Fe-glass seals, vacuum tube construction
2	Calorstea, see Pyrostea				
3	Isostea	Clinoenstatite $MgO \times SiO_2$	Dense	Good for precision work, strong	General electrical equipment
4	Isostea P	Zirconia-magnesium-silicate, $ZrO_2 \times MgO \times SiO_2$	Dense	Good thermal shock resistance[1]	Insulators to take very high mechanical loading
5	PW 23	$Al_2O_3 \times SiO_2$	Finepore	Heat-resistant to 1700 °C	Heater support sleeves refractory crucibles pyrometer tubes (sheaths)
6	Pyrostea	Cordierite $2MgO \times 2Al_2O_3 \times 5SiO_2$	Finepore to dense	Good H.T. insulation resistance	Heater supports, spark or arc killer
7	Rastea	Clinoenstatite $MgO \times SiO_2$	Dense	Low tan δ[1]	

[1] Also low warping, holds dimensions, strong.

SU: Russian ceramics (data from LEBEDINSKIJ)

NO.	DESCRIPTION	CONTENT (w/o)										
		Al_2O_3[2]	Al_2O_3 NORMAL	TALC	$BaCO_3$	$CaCO_3$	MARBLE	$BaCO_3 + B_2O_3$ FRIT	MAGNESITE	CaF_2 FLUORSPAR	BORAZITE[4]	CLAY AND KAOLIN
1	Ultraporcelain UF 53, vacuum-tight	—	65	—	—	—	3	5	3	2	—	Clay[5] 22
2[7]	Steatite, vacuum-tight	1	—	84	10	5	—	—	—	—	—	—
3[7]	Steatite, porous											
4	Steatite B, vacuum-tight	—	—	91	—	—	—	—	—	—	3.2	Kaolin[6] 5.2
5	High-alumina mass no.102, vacuum-tight	60	—	4	8	3	—	—	—	—	—	Clay[5] 25
6	Corundum borazite	94	—	—	—	—	—	—	—	—	6	—
7	Corundum	100	—	—	—	—	—	—	—	—	—	—

[2] Electrocorundum, 99—99.5% Al_2O_3. [3] Talc from Onotsk + 31.7% MgO, 63.5% SiO_2, 4.8% water of crystalization. [4] Borazite = glass, 63.4% B_2O_3, 13% MgO, 18% CaO, firing temperature reduced to 1360—1400°. [5] Clay from Tschasowijarsk, 35% Al_2O_3 and at most 1.3% iron oxides. [6] Kaolin + 40—45% Al_2O_3. [7] Steatite ceramics 2 and 3 have same composition but different firing temperatures.

TABLE T 12–11. PROPERTIES OF COMMERCIAL

Abbreviations:
WA: water absorption
γ: apparent density
Por.: pore volume (for WA = 0: closed; otherwise, closed + open pore vol.)
T_{soft}: softening temperature
T_{safe}: max. working temp.
CFP: cone fall point (refractoriness)
T_{fire}: firing temp.
σ_{zB}: tensile strength;
σ_{dB}: compress. str.;
σ_{bB}: bend strength;
a_n: impact bend strength

[12.3]

TABLE T 12–11A. American ceramics.

NO.	TRADE NAME	TYPE	WA [%]	γ [g/cm³]	T_{soft} [°C]	T_{safe} [°C]
1	Alsimag 35	Steatite	0—0.02	2.5	1450	1000
2	Alsimag 178	Cordierite	10—15	Like Alsimag 202		
3	Alsimag 196	Steatite	0—0.02	2.6	1440	1000
4	Alsimag 197	Steatite	0.02—1	2.6	1445	1000
5	Alsimag 202	Cordierite	10—15	2.1	1430	1250
6	Alsimag 206	Steatite	0—0.02	Like Alsimag 35		
7	Alsimag 207	Steatite	0—0.02	Like Alsimag 35		
8	Alsimag 209	Steatite	0.02—1	Like Alsimag 197		
9	Alsimag 210	Steatite	0.02—1	Like Alsimag 197		
10	Alsimag 211S	Steatite	0—0.1	2.7	1400	1100
11	Alsimag 222	Mg-silicate	14—18	2.0	1625	1300
12	Alsimag 228	Steatite	0—0.02	2.7	1440	1000
13	Alsimag 243	Forsterite	0—0.02	2.8	1440	1000
14	Alsimag 393	Al-silicate	12—18	2.4	1800	1400
15	Alsimag 475	Zr-silicate	0—0.02	3.7	1440	1100
16	Alsimag 504	Zr-silicate	8—14	2.9	1610	1350
17	Alsimag 508	ZrO_2	12—16	2.9	2400	1600
18	Alsimag 513	Al-silicate	0.00	Like Alsimag 576		
19	Alsimag 544	93% Al_2O_3	10—12	2.6	1800	1400
20	Alsimag 547	Cordierite	2—7	Like Alsimag 202		
21	Alsimag 548	100% Al_2O_3 (porous!)	14—17	2.4	2050	1620
22	Alsimag 576	85% Al_2O_3	0.00	3.4	1440	1100
23	Alsimag 614	96% Al_2O_3	0.00	3.7	1650	1550
24	Alsimag 652	98% Al_2O_3	0.00	3.8	1700	1600
25	Lava Grade A	Al-silicate	2—3	2.3	1600	1100
26	Lava 1136	Mg-silicate (soapstone)	2—3	2.8	1475	1250
27	Lava 1137					

SILICATE CERAMICS

E:	Young's modulus	c_{20-100}:	mean specific heat between 20° and 100 °C
G:	shear modulus	ϱ:	electrical resistivity (volumetric)
H_{Mo}:	Mohs' hardness	Te:	Te value; temperature for 1 MΩ-cm
α:	expansion coefficient	E_d:	breakdown strength
TSR:	thermal shock resistance	ε:	dielectric constant
τ:	thermal diffusivity	$\tan\delta$:	dielectric loss angle
λ:	thermal conductivity		

[12.3]

A 1 Mfr.: AMER. LAVA CORP. (their data)

σ_{zB} [kg/mm²]	σ_{dB} [kg/mm²]	σ_{bB} [kg/mm²]	α_n $\left[\frac{\text{kg cm}}{\text{cm}^2}\right]$	H_{Mo}	α [10^{-7}/°C] 25–300 °C	25–700 °C	λ $\left[\frac{\text{cal}}{\text{cm s °C}}\right]$
6	56	12.5	4.2	7.5	80	87[17]	0.006
7	63	14	4.7	7.5	98	86[17]	0.006
6	53	14	4.2	7.5	111	102[17]	0.006
2.5	21	5.6	2.4	7	22	28[17]	0.003
—	46	12.5	3.8	7.5	68	85	
1.8	7	3.5	1.8	6	89	100[17]	0.005
7	63	14	3.8	7.5	80	89[17]	0.006
7	60	14	3.8	7.5	100	112[17][18]	0.008
—	7	(7)	2.8	—	60	72[17]	0.004
8.4	70	13	5.2	8	36	41[17]	0.012
—	14	9	4.7	—	54	53[17]	0.003
—	7	2.8	3.8	—	96	99[17]	0.004
—	39	10.5	3.8	—	62	74	0.004
—	7.3	5.6	2.8	—	69	82	see Fig. B 12-65A
14	98	28	5.9	9	65	75[17]	0.040
18	280	54	6.6	9	65	79[17]	0.045
18	294	44	6.6	9	65	80[17]	0.045
1.8	28	6.3	3.1	6	33	36[17]	0.003
—	28	6.3	—	6	107	119[17]	0.005

TABLE T 12–11A *(continued)*.

NO.	TRADE NAME	ϱ [Ω-cm]				
		100 °C	300 °C	500 °C	700 °C	900 °C
1	Alsimag 35	2.1×10^{12}	6×10^{7}	3.2×10^{5}	2.3×10^{4}	7×10^{3} (12)
2	Alsimag 178	Like Alsimag 202				
[12.3] 3	Alsimag 196	1×10^{13}	6.5×10^{9}	4×10^{7}	1.8×10^{6}	3×10^{5}
4	Alsimag 197	8.1×10^{13}	2.5×10^{10}	8.8×10^{7}	4.2×10^{6}	6.8×10^{5}
5	Alsimag 202	3×10^{13}	2×10^{10}	9×10^{7}	3×10^{6}	3.5×10^{5}
6	Alsimag 206	Like Alsimag 35				
7	Alsimag 207	Like Alsimag 35				
8	Alsimag 209	Like Alsimag 197				
9	Alsimag 210	Like Alsimag 197				
10	Alsimag 211 S	$> 10^{14}$	$> 10^{14}$	9×10^{8}	1×10^{7}	1.5×10^{6}
11	Alsimag 222	$> 10^{14}$	6×10^{11}	4.6×10^{9}	1.7×10^{8}	1.1×10^{7}
12	Alsimag 228	$> 10^{14}$	8×10^{10}	3×10^{8}	5×10^{6}	4×10^{5}
13	Alsimag 243	5×10^{13}	7×10^{11}	1.2×10^{10}	1×10^{8}	3×10^{6} (12)
14	Alsimag 393	5×10^{12}	1×10^{10}	7.5×10^{7}	3.6×10^{6}	5.6×10^{5} (12)
15	Alsimag 475	2×10^{13}	5.5×10^{11}	5.5×10^{8}	1.4×10^{7}	8.2×10^{5}
16	Alsimag 504	$> 10^{14}$	3.6×10^{9}	1.8×10^{7}	1×10^{6}	2.2×10^{5}
17	Alsimag 508	$> 10^{14}$	4.5×10^{9}	8.2×10^{6}	2.5×10^{5}	4×10^{4}
18	Alsimag 513	Like Alsimag 576				
19	Alsimag 544	$> 10^{14}$	1.7×10^{10}	6.1×10^{7}	4.2×10^{6}	8.6×10^{5}
20	Alsimag 547	Like Alsimag 202				
21	Alsimag 548	$> 10^{14}$	$> 10^{14}$	1×10^{10}	2.7×10^{8}	8×10^{7}
22	Alsimag 576	2×10^{13}	5×10^{10}	1×10^{8}	3×10^{6}	4×10^{5}
23	Alsimag 614	2×10^{13}	6×10^{11}	1×10^{9}	4×10^{7}	3×10^{6} (12)
24	Alsimag 652	3.4×10^{12}	1.4×10^{10}	3.4×10^{8}	1.8×10^{8}	6×10^{7}
25	Lava Grade A	6×10^{11}	2×10^{9}	5×10^{6}	3.5×10^{5}	5×10^{4} (12)
26	Lava 1136	9×10^{12}	1.2×10^{10}	1.1×10^{8}	3.3×10^{6}	4.2×10^{5} (12)
27	Lava 1137					

(1) 350 °C: 5.9.
(2) 200 °C: 8×10^{-4}, 350 °C: 15×10^{-4}.
(3) 200 °C: 5.7.
(4) 200 °C: 20×10^{-4}, 350 °C: 80×10^{-4}.
(5) At 10^{8} c/s.
(6) 1.5 mm thickness of test-piece, unlike the others which were 6 mm thick.
(7) 350 °C: 5.9.
(8) 200 °C: 13×10^{-4}, 350 °C: 70×10^{-4}.
(9) 350 °C: 5.7.

A 1 Mfr.: AMER. LAVA CORP. (their data)

T_e	E_d (6 mm)	ε			$\tan\delta$ [10^{-4}]		
[°C]	[kV/cm]	60 c/s	10^6 c/s	10^{10} c/s	60 c/s	10^6 c/s	10^{10} c/s
440	90	6.1	5.9[11][14]	5.5	150	35[11][14][15]	54
750	96	5.9	5.8[11][14]	5.3	22	21[11][14][15]	20[16]
840	84	6.3	6.0	5.7[5]	20	12	9[5]
780	40	—	5.8	4.9[5]	—	40	30[5]
930	96		5.8[1]			7[2]	
> 1000	20	—	5.5	5.5[5]	—	2	2[5]
820	96	6.2	6.1[11][13][14]	5.8	13	13[11][13][14][15]	14[16]
> 1000	96	6.3	6.2[11][14]	5.8	14	4[11][14][15]	10[16]
835	20	—	5.5[9][11]	5.3[5]	5[10]	5[5][11][15]	[16]
870	100	9.1	8.8	8.4	360	10	27
700	—	—	—	—	—	—	—
610	—	—	—	—	—	—	—
875	20	—	5.5	—	—	25	—
> 1000	20		5.5[3]			5[4]	
800	100	8.4	8.3	8.0	13	7	15
930	120[6]	—	9.3	9.1	—	3	14
> 1000	120[6]	—	9.4	9.2	—	3	8
620	32	—	5.3	5.2[5]	—	100	70[5]
810	40	—	5.8[7]	—	—	3[8]	—

[12.3]

[10] 200 °C: 20×10^{-4}, 350 °C: 80×10^{-4}.
[11] See also Table T 12–12.
[12] Fig. B 12-18A.
[13] Fig. B 12-27.
[14] Fig. B 12-28.
[15] Fig. B 12-29.
[16] Fig. B 12-32.
[17] Fig. B 12-33.
[18] Fig. B 12-38.

TABLE T 12–11A *(continued)*

TABLE T 12–11A *(continued)*

TABLE T 12–11A *(continued)*

[12.3]

NO.	TRADE NAME	TYPE	WA [%]	γ [g/cm³]	POR [%]	T_{soft} [°C]	σ_{zB} [kg/mm²]	σ_{dB} [kg/mm²]	σ_{bB} [kg/mm²]	a_n $\left[\frac{\text{kg} \cdot \text{cm}}{\text{cm}^2}\right]$
1	Almanox 2570	Zr-Mull.	0	2.84	11.9	1649	3.4	55	14	4.0
2	Almanox 3569	Zr-Sil.	0	3.08	12.9	1549	4.9	44	12.6	4.8
3	Almanox 4462	Al-Sil.	0	3.52	9.3	1927(1)	11	131	25	5.8
4	Almanox 5301	Cord.	8.5	2.00	19.4	1410	1.7	41	4.3	2 1
5	Almanox 6096	Al-Sil.	0	3.44	4.7	1971	9.2	101	21	5.5
6	Almanox 7873	Al-Mull.	0	2.97	10.9	1649	7.5	84	20	4.8
7	Almanox 11858	Porcel.	0	2.37	5.4	1554	2.3	50	7.7	2.4
8	Almanox 13889	Steat.	0	2.68	6.5	1388	5.3	52	12	4

(1) $T_{safe} \approx 1500$ °C. (2) 600 °C. (3) 300 °C. (4) 200 °C: 8.2×10^7 Ω-cm, 300 °C: 4×10^6 Ω-cm.

TABLE T 12–11C

TYPE	T_{fire} [°C]	σ_{zB} [kg/mm²]	σ_{dB} [kg/mm²]	σ_{bB} [kg/mm²]	α [10^{-7}/°C] 20—700 °C
Electroporcelain Louny	1380	4	38	6	46
Steatite	1300	—	60	14	83
Forsterite	1380	—	—	—	106
Al-sil. (corundum)	1700	—	200	28	76

	γ [g/cm³]	Por. [%]	T_{safe} [°C]	σ_{dB} [kg/mm²]	σ_{bB} [kg/mm²]	a_n [kg cm/cm²]
Porolit(3) (4)	2.04 1.55(6)	25.9 40(6)	> 1410	≈ 12(6)	3.9	1.75
Porolit(5)	1.4—1.7(6) 1.9—2.1(7)	39—41(6) 24—28(7)		10—18	3.2—5.5	1.6—2.0

(1) 10^8 c/s: 8.1. (2) 10^8 c/s: $< 0.3 \times 10^{-4}$. (3) Machinable porous steatite. (4) Mean values.

A 2 Mfr.: BELL TELEPHONE LAB.: see Table T 12–12

A 3 Mfr.: COORS PORCELAIN Co.: see Table T 12–12

A 4 Mfr.: FRENCHTOWN PORCELAIN Co. (their data)

α [10^{-7}/°C] 25–100 [°C]	25–400 [°C]	75–700 [°C]	λ [cal/cm s °C]	ϱ [Ω-cm] 400 °C	500 °C	700 °C	800 °C	Te [°C]	E_d (6 mm) [kV/cm]	ε 10^6 c/s	tan δ [10^{-4}] 10^6 c/s
20	34	38	0.0062	1.5×10^{8}(3)	1.6×10^{6}	$4\cdot10^{5}$(2)	—	527	100	5.9	32
29	41	45	0.0072	1.4×10^{8}	1.8×10^{7}	8×10^{5}	—	677	84	7.1	17
36	61	73(6)	0.0180	2×10^{8}	5.3×10^{7}	3.8×10^{6}	1×10^{6}	799	82	9.2	3.5(5)
23	30	30	0.0045	8.6×10^{7}	1.7×10^{7}	1.4×10^{6}	7×10^{5}	743	26	3.5	82
53	69	74	0.0144	2.2×10^{8}	3.4×10^{6}	1.8×10^{6}	6×10^{5}	749	81	8.4	8.6
44	57	64	0.0095	1.3×10^{8}	2.5×10^{7}	1.2×10^{6}	4×10^{5}	710	80	7.0	14
41	54	60	0.0047	$3\cdot10^{5}$(4)	—	—	—	349	88	5.4	85
55	66	73	0.0057	1.4×10^{8}	1.2×10^{7}	4×10^{5}	—	632	79	5.9	19

[12.3]

(5) 10^2 c/s: 24×10^{-4}, 10^{10} c/s: 15×10^{-4} (see also Table T 12–12). (6) See also Fig. B 12-40.

ČSSR (Czech) ceramics (approx. values)

ε 50 c/s	10^6 c/s	10^7 c/s	tan δ (10^{-4}) 50 c/s	10^6 c/s	10^7 c/s
6.6	6.9	6.5	350	87	78
6.9	7.2	7.2	5	9	7.5
—	8.2	8.1(1)	—	3	2(2)
9.9	10.1	10.1	90	18	12

α [10^{-7}/°C]	λ [cal/cm s °C]	TSR [°C]	ϱ [Ω-cm] 20 °C	600 °C	R_{00} [Ω]	ε 10^6 c/s	tan δ (10^{-4}) 10^6 c/s
74	0.001	372	7×10^{13}	2×10^{7}	3×10^{12}	4.8	6.3
70—80	0.0009—0.0011	330—420	10^{12}—10^{13}		10^{11}—10^{12}	4—5	4—8

(5) Limiting values. (6) Values for extruded material. (7) Values for molded material.

TABLE T 12–11D.

α) Mfr. and

MFR.	DIN TYPE						
	110	111	120	210	220	221	240
DEGUSSA, Frankfurt a. Main							
[12.3] DÖBRICH UND HECKEL, Lauf-Pegnitz					Steatite	E 7	
HALDENWANGER, Berlin-Spandau	Porcelains						
VEB KERAMISCHE WERKE (HESCHO), Hermsdorf/Thüringen	Hard porcelains				Steatite	Calit	
KLOSTER VEILSDORF VEB, Veilsdorf i. Thür.	High-fired porcelains						
KOPPERS, Düsseldorf-Heerdt							
VEB KERAMISCHE WERKE, Neuhaus-Schierschnitz i. Thür.	H.V. porcelain 110	Molded porcelain 111		Steatite 210	Steatite 220	Elit 221	Steatite 240
PHILIPS KERAMISCHE WERKE, Hamburg-Langenhorn	Hard porcelain					K 6 (Deltan)	(Kerpora)
ROSENTHAL-ISOLATOREN GMBH, Selb/Oberfranken	Hard porcelain	Molded porcelain				Rosalt 7	
SEMBACH u. Co., Lauf/Pegnitz					Steatite	Stealan	
SIEMENS-SCHUCKERT, Porzellanfabrik, Hochstadt/Oberfranken						Elit	
STAATLICHE PORZELLAN-MANUFAKTUR BERLIN, Werk Selb/Oberfr.	Berlin hard porcelain						
STEATIT MAGNESIA, Lauf/Pegnitz	Melalith				Steatite	Frequenta M	Ergan
VEB ELEKTROKERAMIK "ARTHUR WINZER", Berlin-Pankow		ELKApan			Steatite	ELKAfret	ELKAvac S
STETTNER u. Co., Lauf/Pegnitz					Steatite	Stettalit (D 6)	Stettalit, annealed
WITTEN-ELEKTROKERAMIK, Witten			Ardorit 6, 18	Ardorit 12			

German Ceramics

Trade Name (see also STOLL)

AS PER TABLE T 12–10 D

410	510	511	512	520	530	610	710	720/730
						"Degussit" (see Table T 12–26A) D, K, DD	AL 23, AL 24, AL 25	BE, MG, SP, TH, ZR [12.3]
				Heater element base				
	Schamotte, M, R			Sillimanit 60, SKK		Pytagoras-Masse	Alsint	
Ardostan					Thermisol		Pyrodur	
						Sillimanit 10 a, H, HE	Clay body TE	
Liborit 410	Thermolan 510			Thermolan 520	Ignolan 530, Thermodur 530	Elkorit 610, Ignodur 610, Pyrolan 610[1]	Sintered corundum 710	
		Th 11						
Rosaltherm I				Rosaltherm III			Rosaltherm II	
				Pyrostat				
						K-Masse	Prokorund	E-Masse
Sipa H	Q 5 up to 1000°		ST. GN, up to 1000°	Sipa, up to 1200°	Sipalox, up to 1300°			
	ELKAwit		ELKAtherm	ELKAdur	ELKAlox			
		Stetta H 1		Stetta E 12	Stetta G			
	Ardorit I (fine-pore)		Ardorit II (coarse-pore)					

[1] Other products in this group: Thermodur 611, Ignolan 631.

TABLE T 12–11D

β) Properties of German standardized ceramics,

DIN TYPE	TYPE	WA [%]	γ [g/cm³]	CFP [°C]	σ_{zB} [kg/mm²]	σ_{dB} [kg/mm²]	σ_{bB} [kg/mm²]	a_n [kg cm/cm²]
110	H.V. porcelain	0	2.3—2.5	1670	*3—5*[1] 2.5—3.5	*45—55*[1] 40—45	*6—10*[1] 4—7	1.8—2.2
111	Molded porcelain	0.1—0.5	2.3—2.5	1670	—	30—40[1] 25—35	3—6	1.3—1.6
120	Stoneware	0.4—0.8	2.5	1670	—	40—55[1] 40—45	4—7	1.7—2.1
210	Steatite, low-fired	0.1—0.5	2.8	—	—	80—90	10—12	3—4
220	Ordinary steatite	0	2.6—2.8	—	6—9.5[1] 4.5—6	85—95	12—14	3—5
221	Special steatite	0	2.6—2.8	1460	6—10[1] 4.5—6	90—100	14—16	4—5
240	Mg-silicate, porous	≈ 20	1.9—2.1	1460	—	10—20	3.5—6	1.6—2.2
410	Cordierite, dense	0	2.1—2.2	—	2.5—3.5	30—50	5—8.5	1.8—2.2
510	Porous bodies	5—15	1.9—2.1	1500 to 1710	1—1.5	20—25	4—5	1.7—2.1
511	Porous bodies	5—10	1.9—2.1	1500 to 1710	1—1.5	20—25	4—5	1.3—1.7
512	Porous bodies	15—20	1.8—1.9	1460	0.9—1	5—8	1.5—2	1.3—1.5
520	Cordierite, porous	3—10	≈ 2	1435	1—2	25—30	5—6	1.8—2.2
530	Al-silicate, porous	10—15	2.0—2.1	1730	1—1.5	25—30	4—5	1.7—1.8
610	Al-silicate, dense	0	2.6—3.3	> 1720	4—10	70—150	12—22	4—5
710	Al_2O_3	0	3.7—3.9	2030	26	300	30	3—5
720	MgO	≈ 10	≈ 2.5	2640	—	—	—	—
730	ZrO_2, stabilized	0	5.4	2700	15	210	19	—

[12.3]

[1] Glazed; all other strength values for unglazed ceramics. [2] Sipalox: 25—37.

(continued)

arranged by type (DIN classification)

E $\left[\frac{kg}{mm^2}\right]$	G $\left[\frac{kg}{mm^2}\right]$	H_{Mo}	α [10^{-7}/°C] 20 to 100 °C	20 to 600 °C	20 to 1000 °C	TSR [°C]	τ $\left[\frac{cm^2}{sec}\right]$	λ $\left[\frac{10^{-3}\,cal}{cm\ s\ °C}\right]$	c_{20-100} $\left[\frac{cal}{g\ °C}\right]$
5500 to 8000	2000 to 3000	7—8	35—45	40—45	40—50	160	58—81	2.8—3.9	0.19—0.21
			See Fig. B 12-34						[12.3]
—	—	7—8	35—45	40—50	40—50	—	58—81	2.8—3.9	0.19—0.21
—	—	7—8	47	—	—	—	78	3.4—4.5	0.20
—	—	7—8	68	—	—	—	81	4.2—4.8	0.20
8000 to 11,000	≈ 4000	7—8	70—90	70—90	80—100	80—130	109	5.6—6.7	0.19—0.22
11,000 to 13,000	4000 to ≈ 5000	7—8	60—80	70—90	80—90	110—150	109—112	5.6—6.7	0.19—0.22
			See Fig. B 12-34						
—	—	—	85—95	≈ 90	≈ 90	—	87	3.4—3.9	0.21
9000 to 12,000	≈ 5000	7—8	≈ 10	20—30	20—30	250	112	4.8—5.6	0.20—0.22
—	—	6—7	30—50	40—60	40—60	—	76—101	2.8—4.2	0.19—0.20
—	—	6—7	30—50	40—60	40—60	—	≈ 84	3.1—3.6	≈ 0.20
—	—	6—7	30—50	30—60	30—60	—	≈ 73	2.5—2.8	0.19—0.20
≈ 8000	≈ 3000	6—7	15—30	20—40	25—50	—	76—107	3.1—4.2	0.2
—	—	6—7	35—50 (2)	40—60	40—70	—	90	3.4—3.9	0.19—0.20
10,000 to 11,000	—	8—9	50—60	60—80	70—80	150—160	120—129	5.6—42	0.2—0.25
25,000 to 38,000	—	9	50—70	60—80	70—80	—	364—476	31—39	0.2—0.23
9000	—	6	80—90	110–130	120–140	—	252	19.5	0.23
17,000	—	8	80—90	—	—	—	98	5.6	0.12

TABLE T 12–11D

β) Properties of German standardized ceramics,

DIN TYPE	TYPE	ϱ [Ω-cm]				
		20 °C	200 °C	400 °C	600 °C	800 °C [1000 °C]
110	H.V. porcelain	10^{11}—10^{12}	10^{7}—10^{9}	10^{5}—10^{6}	10^{4}—10^{5}	—
[12.3] 111	Molded porcelain	—	10^{7}—10^{9}	10^{5}—10^{6}	10^{4}—10^{5}	—
120	Stoneware	—	10^{8}	10^{6}	10^{5}	—
210	Steatite, low-fired	—	10^{9}	10^{7}	10^{5}	—
220	Ordinary steatite	5×10^{11} to 5×10^{12}	10^{10}—10^{11}	10^{7}—10^{8}	10^{5}—10^{6}	—
221	Special steatite	10^{12}—10^{13}	10^{11}—10^{12}	10^{9}—10^{10}	10^{7}—10^{8}	10^{6}—10^{7} [10^{5}—10^{6}](1)
240	Mg-silicate, porous	—	—	10^{8}—10^{9}	10^{7}—10^{8}	5×10^{5}—5×10^{6} [10^{5}—10^{6}](1)
410	Cordierite, dense	10^{11}—10^{12}	10^{8}—10^{9}	10^{6}—10^{7}	10^{5}—10^{6}	10^{4}—10^{5}
510	Porous bodies	—	—	5×10^{6} to 5×10^{7}	10^{5}—10^{6}	10^{4}—10^{5} [5×10^{3}–5×10^{4}](1)
511	Porous bodies					
512	Porous bodies					
520	Cordierite, porous	—	—	10^{7}—10^{8}	5×10^{5} to 5×10^{6}	5×10^{4}—5×10^{5} [10^{4}—10^{5}](1)
530	Al-silicate, porous	—	—	10^{7}—10^{8}	10^{6}—10^{7}	10^{5}—10^{6} [10^{4}—10^{5}](1)
610	Al-silicate, dense	—	—	—	—	—
710	Al_2O_3	—	—	—	—	—
720	MgO	—	—	—	—	—
730	ZrO_2, stabilized	—	—	—	—	—

(1) At 1000 °C. (2) Dried (Ergan: 3—8; Ergan at 4×10^{9} c/s: 18×10^{-4}). (3) Dried. (4) 160 °C: *ca.* 12.

(continued)

arranged by type (DIN classification)

E_d [kV/cm]	ε	tan δ [10^{-4}]		tan δ [10^{-4}]			
		20 °C; 50 c/s	20 °C; 10^6 c/s	f	60 °C	80 °C	100 °C
300—500	≈ 6	170—250	60–120	50 c/s	≈ 400	≈ 600	≈ 1200
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
200—300	≈ 6	25—30	15—20	50 c/s	≈ 150	≈ 350	≈ 650
300—450	≈ 6	10—15	3—5 (8—15)	50 c/s 10^6 c/s	40—60 4—5	70—120 5—6	120—150 6—8 (9.5)[4]
—	≈ 4.5	—	2—4[2]	—	—	—	—
100—200	≈ 5	200	40—70	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
250—350	—	—	—	—	—	—	—
—	9	≦ 2	≦ 2	—	—	—	—
—	10	≧	≦ 6[3]	—	—	—	—
—	19	—	—	—	—	—	—

[12.3]

TABLE T 12–11D

γ) Properties of some German ceramics so far

NO.	TRADE DESCRIPTION	COMPOSITION	WA [%]	γ [g/cm³]	σ_{zB} [kg/mm²]	σ_{dB} [kg/mm²]	σ_{bB} [kg/mm²]	a_n [kg cm/cm²]	E [kg/mm²]
1	Zirkon-porzellan	Zr porcelain	0	2.8—3	6—9.5(1) 4.5—6	75—90	10—11	4	8000 to 10,000
2	Frequenta Spezial	Special steatite, contains Zr	0	2.8—3	6—9(1) 4.5—6	90—100	13—15	4—5	—
3	Frequenta Spezial A	Special steatite. contains Zr	0	3—3.2	5—8(1) 4—5	80—90	12—14	4—5	—
4	Frequenta M	Forsterite	0	2.8	4—6(1) 3.5—4.5	80—90	10.5—11.5	3—4	—

[12.3]

(1) Glazed; all other strength values are for unglazed ceramics. (2) Essentially higher

δ) Properties of vacuum-tight ceramics made

NO.	TRADE DES-CRIPTION	DIN GROUP	WA [%]	γ [g/cm³]	LIMITS IN USE IN HV	LIMITS IN USE AT ATM. PRESSURE	σ_{zB} [kg/mm²]
1	Berliner Hart-porzellan	110 111	0	2.46	1100	1400	3.2
2	K-Masse	610	0	2.60	1300	1600	—
3	Prokorund	710	0	3.2	1600	≈ 1700	8.7

(1) Can be sealed to SCHOTT glass Duran No. 8330 (Table T 10–4, D 9) or to Pyrex glass CORNING 7740

TABLE T 12–11E.

α) Mfr. and trade names

MANUFACTURER	TRADE NAMES		
	GROUP	1	2
	TYPE	ELECTROPORCELAINS	STEATITES
BRAY AND CO. LTD.		"45"	"G", "GP", "I", "IP", "Ellain"
BULLERS LTD.		Porcelain	"Frequelex F2", "Frequelex F4"
HACKNEY AND CO. LTD.		Porcelain	No T 222, No 907
KLG SPARKING PLUGS LTD.			
LODGE PLUGS LTD.			
MACINTYRE AND CO. LTD.		Porcelain	LL 3
MORGAN CRUCIBLE CO.			
STEATITE AND PORCELAIN PROD.		Porcelain	Frequentite
TAYLOR TUNNICLIFF LTD.		Porcelain	HF 20
THERMAL SYNDICATE LTD.			
UNITED INSULATOR CO.		"P 7"	S 2, Calit, S 8 C

(continued)

not standardized (data from STEATIT-MAGNESIA A.G.)

H_{Mo}	α [10^{-7}/°C] 20–100 °C	20–1000 °C	TSR [°C]	λ [cal/cm s °C]	ϱ [Ω-cm] 500 °C	1000 °C	E_d [kV/cm]	ε	tan δ (10^{-4}), 20 °C 50 c/s	10^6 c/s
8	29	52	220—280	(2)	10^5—10^6	10^3—10^4	250—350	≈ 6	100–150	40—60
7—8	61	76	130—160	—	—	—	—	≈ 6	10—15	5—8
7—8	59	74	150—180	—	—	—	—	≈ 6	10—15	5—8
7—8	89	106	70—110	—	10^9—10^{10}	10^6—10^7	250—350	≈ 6	10—15	2.3—4

[12.3]

than Melalith (i.e. $> 14 \times 10^{-3}$).

by the STAATLICHE PORZELLANMANUFAKTUR BERLIN, Werk Selb (Ofr.)

σ_{dB} [kg/mm²]	σ_{bB} [kg/mm²]	a_n [kg · cm/cm²]	H_{Mo}	α [10^{-7}/°C] 20—700 °C	λ [cal/cm s °C]	ϱ [Ω·cm] at 900 °C	VACUUM TIGHTNESS
42	8.55	1.99	8	38(1)	3.4×10^{-3}	2.8×10^5	see Table T 12–14
61.8	—	—	8.5	49	5.2×10^{-3}	4.9×10^5	
119	19.5	4.86	9	55	18×10^{-3}	1.1×10^6	

(see Table T 10–4, A 1)

BRITISH CERAMICS

(B.I.R.E. data)

TRADE NAMES		
3	4	5
FORSTERITES	CORDIERITES	AL-SILICATES
Forsterite No. 352	Cordalex HR 129, HR 133	Hylumina Sintox (95w/o Al_2O_3) Triangle (recryst. Al_2O_3)
	252	Thermal (recryst. Al_2O_3)

TABLE T 12–11 E

β) Properties of British ceramics,

GROUP	TYPE	γ [g/cm³]	POR. [%]	T_{safe} [°C]	σ_{zB} [kg/mm²]	σ_{dB} [kg/mm²]	σ_{bB} [kg/mm²]
1	Porcelains	2.3—2.5	0—2	900—1000	1—5	15—90	3—15
2	Steatites	2.6—2.9	0—0.1	1000—1100	2.1—5.6	35—125	7—17.5
[12.3] 3	Forsterites	2.8—3.0	0—0.1	1000	6.5—7.5	55—65	12.6—14
4	Cordierites	2.0—2.4	0—10	1200—1250	1—2.5	15—30	1.2—5
5	Al-silicates (Al_2O_3)	3.7—3.9	0	1250—1950	12—26	160—300	20—30

(1) Tested per Brit. Standard B.S. 1598:1949.

TABLE T 12–11 F.

Mfr.: COMP. GEN. D'ELECTRO-CERAMIQUE

NO.	TYPE	σ_{zB} [kg/mm²]	σ_{dB} [kg/mm²]	σ_{bB} [kg/mm²]	E [kg/mm²]
1	Electroporcelains	4	50	8	7000
2	Steatite, low-loss	6.5	60	12	10,000
3	Al-silicates, 50% Al_2O_3	—	80	13	12,000
4	Al-silicates, 66% Al_2O_3	8—10	100	20	13,000
5	Al-silicates, 95% Al_2O_3	18	200	35	25,000
6	Sintered Al_2O_3	29	—	—	34,000

TABLE T 12–11 S.

S 1 Mfr.: SCHWEIZER ISOLA WERKE

NO.	TRADE NAME	TYPE	γ [g/cm³]	σ_{zB} [kg/mm²]
1	Alphastea	Forsterite, dense	2.65	4.5
2	Calorstea	Cordierite, porous	2.4	3
3	Isostea	Steatite, dense	2.75	5
4	Isostea P	Zr-silicate, dense	3.1	6
5	PW 23	Al-silicate, fine-pore	2.0	2
6	Pyrostea	Cordierite, porous	2.4	3
7	Rastea	Steatite, dense	2.74	5.5

(continued)

arranged by group

a_n $\left[\frac{\text{kg cm}}{\text{cm}^2}\right]$	α [10^{-7}/°C]	ϱ [Ω-cm] 20 °C	300 °C	600 °C	E_d(1) [kV/cm]	ε at 10^6 c/s	tan δ [10^{-4}] 10^6 c/s	
0.5—1.5	30—60	10^{14}—10^{16}	5×10^6—10^8	10^4—10^6	20—200	5—7	50—100	
0.3—5	70—95	10^{13}—10^{17}	3×10^7—10^{10}	10^5—10^8	100—250	6—6.9	5—35	
3.5—4.5	85—125	10^{13}—10^{15}	—	—	90—100	6.2—6.4	1.5—3	[12.3]
0.2—2.5	10—20	10^{15}—10^{17}	10^7—10^9	10^5—10^6	30—80	4.5—5.5	50—100	
2.5—3.5	60—90	10^{13}—10^{16}	10^{10}—10^{14}	10^{10}	100—200	9—10	6—10	

FRENCH CERAMICS
(GALLET)

α [10^{-7}/°C]	λ [cal/cm s °C]	E_d [kV/cm]	ε 25 °C, 10^6 c/s	tan δ [10^{-4}] 25 °C, 10^6 c/s	120 °C, 10^6 c/s
65	0.0035	> 200	6	90	260
75	0.0035	> 200	6	6	30
50	—	150	7	10	—
60	≈ 0.01	> 150	7	6	40
70	0.03—0.05	> 200	8	< 5	< 10
80	≈ 0.05	> 200	9	< 5	<10

SWISS CERAMICS
(WOLF)

σ_{dB} [kg/mm²]	σ_{bB} [kg/mm²]	a_n $\left[\frac{\text{kg cm}}{\text{cm}^2}\right]$	α [10^{-7}/°C]	E_d [kV/cm]	tan δ [10^{-4}] 10^6 c/s
80	10	2.6	95	200	20
40	7	2.2	22	100	—
90	12	2.9	70	250	15
100	16	3.5	57	250	40
35	6	2.0	55	60	—
40	7	2.2	22	100	—
100	12	3.0	70	250	< 8

TABLE T 12–11 SU. RUSSIAN CERAMICS (LEBEDINSKIJ)

NO.	TYPE	WA [%]	γ [g/cm³]	T_{fire} [°C]	σ_{bB} [kg/mm²]	a_n [kg cm/cm²]	α [10^{-7}/°C] 20—200 °C	TSR NO.	λ [cal/cm s °C]	ϱ [Ω-cm] 100 °C	200 °C	300 °C	ε AT 10^6 c/s	tan δ [10^{-4}] AT 10^6 c/s 20 °C	100 °C	300 °C
1	Ultraporcelain UF 53	0		1360			50—55	—	—	3×10^{13}	—	—	8—8.5	3—5	4—6(1)	—
2	Steatite, dense	0		1330			70—75	1(3)	0.0048	—	8×10^{12}	—	5—7	5	—	13
3	Steatite, porous	10–15		1250			72	3(3)	0.0036	10^{13}	—	5×10^{11}	4—5	0.115	2—4	—
4	Steatite B, dense	0		1290			75—85	5(4)	—	—	—	—	5.5–6.5	9(2)	—	—
5	Al-silicate No. 102	0		1380			50—55	10(3)	—	10^{13}	—	—	7.5	8	—	30
6	Corundum-Borazite															
7	Corundum	10–15					55	—	0.020	10^{13}	—	10^{12}	5—6	0.5—1	2.5—5	—

(1) At 80 °C. (2) At 3×10^9 c/s. (3) Number of quenchings in water at 20 °C that a test-piece heated rapidly to 800 °C will withstand without fracture. (4) As (3), but heated to 600° only.

TABLE T 12–12. DIELECTRIC CONSTANT ε AND LOSS ANGLE TAN δ (units of 10^{-4}) OF SOME COMMERCIAL CERAMICS AT VARIOUS FREQUENCIES (FROM HIPPEL). FREQUENCY IN c/s.

	T [°C]		10^2 c/s	10^3 c/s	10^4 c/s	10^5 c/s	10^6 c/s	10^7 c/s	10^8 c/s	3×10^8 c/s	3×10^9 c/s	10^{10} c/s	2.5×10^{10}
A1 Mfr.: AMER. LAVA CORP., Chattanooga/Tenn. (USA)													
Alsimag 35 (ordinary steatite) (3) (5)	23	ε	6.10	5.96	5.89	5.86	5.84	5.80	5.75	—	5.60	—	5.36
		tan δ	150	100	70	50	38	35	37	—	41	—	58
	85	ε	6.84	6.37	6.11	5.96	5.86	5.80	5.75	—	5.50	—	—
		tan δ	890	370	175	103	77	50	50	—	47	—	—
Alsimag 196 (steatite with low-losses) (3) (5)	25	ε	5.90	5.88	5.84	5.80	5.70	5.65	5.60	—	5.42	5.24	5.18
		tan δ	30	59	79.5	55	30.5	19	16	—	18	26	38
	81	ε	5.90	5.88	5.84	5.80	5.70	5.65	5.60	—	5.42	—	—
		tan δ	58	40	46.5	70.5	66	40.5	24	—	18	—	—

Alsimag 228 (very low-loss steatite) (3) (4) (5)	25	ε	6.40	6.40	6.40	6.40	6.36	6.30	6.20	—	5.97	5.93	5.83
		tan δ	15.6	20	20	15.6	12.4	11.2	10	—	13	19.5	42
	81	ε	0.52	6.46	6.40	6.40	6.36	6.30	—	—	5.95	—	—
		tan δ	35.6	22	18	21.5	18.4	11.8	—	—	11	—	—
Alsimag 243 (Forsterite) (3) (5)	22	ε	6.30	6.30	6.28	6.25	6.22	6.17	6.10	—	5.78	5.76	5.75
		tan δ	12.5	4.5	4.0	—	3.7	3.5	3	—	6	8.5	12
	85	ε	6.37	6.37	6.37	6.36	6.32	6.28	—	—	5.88	—	—
		tan δ	21	13.7	8	—	3.7	3.5	—	—	6	—	—
Alsimag 393 (alumina, porous, for electron tube components(5))	24	ε	4.93	4.95	4.95	4.95	4.95	4.95	4.95	—	—	4.95	4.91
		tan δ	38	23	16	12	17	10	10	—	—	9.7	14
A 2 Mfr.: Bell Telephone Labor., New York, N.Y., USA													
Ceramic F–66(2) (5)	25	ε	6.22	6.22	6.22	6.22	6.22	6.22	6.22	—	6.22	—	6.2
		tan δ	14.5	9	5	2	1	1.5	3	—	5.5	—	11
A 3 Mfr.: Coors Porcelain Co., Golden, Colorado, USA													
AB-2 Alumina	25	ε	8.22	8.18	8.17	8.17	8.16	8.16	8.16	—	8.14	8.08	—
		tan δ	20	13.4	11.4	10.5	9	7.5	9	—	16	27	—
AI 200 Alumina	25	ε	8.83	8.83	8.82	8.80	8.80	8.80	8.80	—	8.79	8.79	—
		tan δ	14	5.7	4.8	3.8	3.3	3.2	3.0	—	10	18	—
Zi-4 Zircon porcelain(5)	25	ε	6.44	6.40	6.35	6.32	6.32	6.30	6.30	6.30	6.23	6.18	—
		tan δ	59	40	31	27	23	21	25	27	45	57	—
A 4 Mfr.: Frenchtown Porcelain Co., Trenton, N.J., USA													
Almanox 4462 (alumina)	25	ε	8.99	8.95	8.95	8.95	8.95	8.95	8.95	8.93(71)	8.90	8.80	
		tan δ	22	9.1	6.0	3.0	2.0	2.0	4.0	9(71)	11	14	

(1) At 10^9 c/s. (2) 60% talc, 15% kaolin, 17.5% $BaCO_3$. (3) See also Fig. B 12-28. (4) See also Fig. B 12-27 (5) See also Fig. B 12-29.

12.3.I. *Hard Porcelains (High-fired Porcelains)*

(BUDNIKOW, HECHT, LIEBSCHER, PALATZKY, ROSENTHAL, SALMANG)

"Hard porcelains" in German usage refers only to dense, feldspar Al-silicates, whereas in English the term refers quite generally to dense ceramics (e.g. "steatite porcelain"). We refer here (German usage) to ceramics based on the ternary system $K_2O(Na_2O)$—Al_2O_3—SiO_2. Raw materials for manufacture of hard porcelain are clays (kaolin, etc.), quartz sand ($\geq$ 99.8% SiO_2) and feldspar, in rather variable ratios whose range can be seen from Fig. B 12-35. Table T 12–13 gives some numerical data on the composition [12.3]

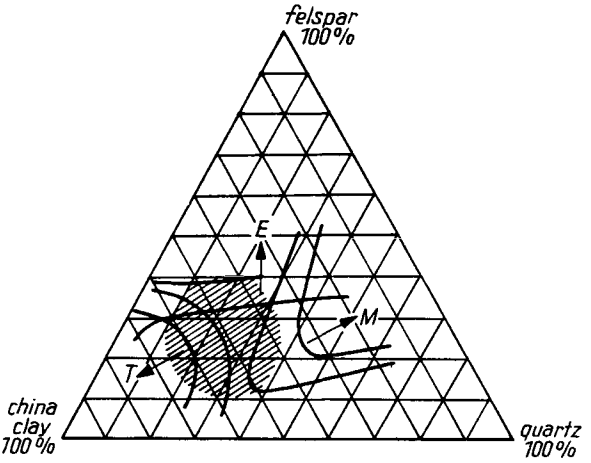


Fig. B 12-35 Percentage composition dependence of some properties of porcelain. Hatched area: classical types of European hard porcelains

E is direction of high electrical breakdown strength
M is direction of high mechanical strength
T is direction of high hot strength
The diagram shows that the three chief strength properties unfortunately cannot be optimally combined in one porcelain

of the raw materials for a few typical hard porcelains. The clay materials are blunged with water and additions are made of quartz sand and feldspar, usually ball-milled (also partly vibro-milled) down to about 50 μ max. grain size; fineness of milling is judged in practice by the amount of so-called "sieve residue" (sieve is mostly 10,000 mesh/cm^2); a typical case would be a residue of 2–4%. Blunging produces a kneadable or castable mass which, as already described in 12.1.III, is worked up to shape by throwing, molding or slip-casting. After pre-drying the piece, firing generally follows in two stages: a first bake at 900–1000° (possibly followed by glazing) and a finishing burn at 1400–1440°. The feldspar now softens, melts and dissolves part of the quartz to form a viscous glass flux. The kaolinite ($Al_2O_3 \cdot 2\,SiO_2 \cdot 2\,H_2O$) at first decomposes to metakaolinite ($Al_2O_3 \cdot 2\,SiO_2$) which then partly converts to mullite ($3\,Al_2O_3 \cdot 2\,SiO_2$). In high-fired porcelain, these mullite crystals can be detected as spicular needles (see, e.g., Fig. B 12-35 D).

The fully-fired hard porcelain finally consists, according to SALMANG, of up to 6–8% undissolved quartz fragments, up to 26% mullite and more than 66% feldspar-silica-glass of the following approximate composition:

SiO_2	Al_2O_3	K_2O (Na_2O)
77–83	12–16	3–7 w/o

The solidification point of this base glass is about 780°, $\alpha = (70 - 104) \times 10^{-7}$/°C (20–780°) (SINGER). A larger quartz content is possible, up to 50%, but not if the porce-

TABLE T 12-13. EXAMPLES OF COMPOSITION OF RAW STARTING MATERIALS FOR HARD PORCELAINS (ROBINSON)

NO.	TYPE OF PORCELAIN	RAW MATERIAL (w/o)				
		KAOLIN		QUARTZ SAND		FELDSPAR
	GERMAN PORCELAIN					
1	Normal values	50		25		25
2	Limits	42–66		12–30		17–37
	AMERICAN PORCELAIN	BALL CLAY	CHINA CLAY (KAOLIN)	FLINT (SAND)	FELDSPAR	WHITING(1)
3	Electro-porcelain	15–35	25–35	15–25	28–38	0–3
4	Chemical porcelain	0–5	50–58	–	20–5	0–1
5	Vacuum-tight porcelain(2)	15	40	20	25	–

[12.3]

(1) Whiting = $CaCO_3$ raws (calcite, marble, chalk, calcium carbonate).

(2) According to HURSH, for betatron tubes similar to Fig. B 12-57; α (10^{-7}/°C) as follows:

25–300°	25–400°	25–500°	25–600°
49.4	52.0	54.7	59.1

Can be sealed very well to CORNING glass 7050 (Table T 10–4, A1). A suitable glaze for this porcelain (with $\alpha = 56 \times 10^{-7}$/°C approx., between 25 and 600°) has the composition:

$$\left.\begin{matrix} 0.20\ K_2O \\ 0.40\ CaO \\ 0.10\ MgO \\ 0.30\ ZnO \end{matrix}\right\} 3.5\ SiO_2 \cdot 0.20\ B_2O_3 \cdot 0.35\ Al_2O_3.$$

lain is to be higher quality. A case in point, porcelain fired at 1400° for 1 hr, made from 50% kaolin, 25% quartz, 25% feldspar, is given by [2]DIETZEL, the composition being

QUARTZ RESIDUE	MULLITE	GLASS
15–25	25–35	40–60 w/o

The best porcelains often consist exclusively of mullite and a glass phase, the quartz being fully dissolved.

Figures B 12-35A–D show microsections of hard porcelains and illustrate better than any detailed explanation the internal structure of this kind of ceramic. Figure B 12-35E shows a microsection of a porcelain with a surface glaze.

By altering the composition of the starting material and the firing process, it is possible within certain limits to vary the ratio of glass phase to crystalline phase. Glass-rich porcelains have an enhanced electrical breakdown strength, crystalline-rich ones are stronger mechanically. Taken as a whole, analysis of porcelain gives the following composition (ROBINSON):

SiO_2	Al_2O_3	K_2O	Na_2O	$Fe_2O_3 + TiO_2 + MgO + CaO$
66–75	19–25	2.5–4	0.5–2	0.5–3 w/o

If firing is undertaken in coal- or gas-fired kilns—as is usually the case—care should be taken, by ensuring an oxidizing atmosphere up to the onset of sintering, that carbon that may be distilled from the fuel and deposited is burnt off. Nevertheless, gas-fired porce-

lain normally always contains about 0.008 to 0.015% C. After this point, the atmosphere must be a reducing one to reduce traces of Fe_2O_3 (which are always present) to FeO, since red Fe_2O_3 even in small amounts will discolor the shards and glaze, but in the presence of traces of black-to-gray FeO, the porcelain remains white.

[12.3]

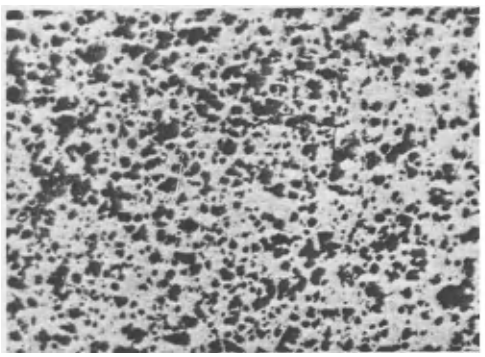


Fig. B 12-35A Porcelain: microsection, top illumination, perpendicul ar bright background illumination (from VÜEK), mag. × 100

Dark regions: partly surface pores opened by polishing, partly also pores filled with colorless, clear glass

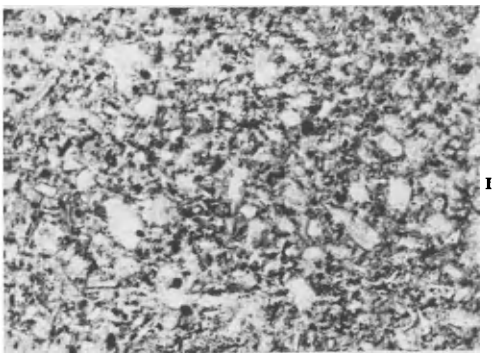


Fig. B 12-35 B I Porcelain: thin section (from VÜEK), mag. × 100

Photograph taken by ordinary transmitted light; circular white pores are bubbles in zones of high concentration of glass phase (in the surroundingcoarse feldspar grains)

The firing shrinkage of porcelains is 12–25% overall, and since the amount cannot be exactly predicted, porcelain cannot be made to an accuracy of better than $\pm 2.5\%$ without finish-grinding (see also 12.1.III).

Because of its high glass content, hard porcelain is very similar in many of its properties to technical glasses, especially at high temperatures. Porcelain is inferior in mechanical strength to the predominantly crystalline ceramics of the steatite group. High temperature strength is determined by the T_{soft} of the feldspar glass which lies roughly between 700° and 800°; porcelain rods clamped at one end and loaded at the other sag noticeably at 800° and to a considerable degree at 1000°. Glaze layers naturally soften sooner, but usually only adhere at temperatures above 950°. The α of porcelain is relatively low, since both mullite and feldspar glass of high silica and alumina content exhibit low expansion. Since α of feldspar porcelain generally lies between 35 and 45 (10^{-7}/°C), i.e. in the same range as that of technical hard glasses, porcelains can be sealed to make good vacuum-tight joints with a corresponding hard glass match (see Chapter 32). In keeping with the small α, the thermal shock resistance of ordinary porcelain is relatively good.

The high glass content means that, even without glazing, porcelain is exceptionally vacuum-tight up to temperatures of 1300° or so. Special ceramics, such as Type K 84 of the STAATLICHE PORZELLAN MANUFAKTUR, Berlin, should be vacuum-tight even up to 1500° (SALMANG). At higher temperatures, the material is slightly permeable to He

and H_2, but as can be seen from Table T 12–14, the permeability is much less than that of ceramics whose glass-phase content is less (see col. 4) or zero (see col. 5). Cf. 12.2.XIV for the transparency of porcelain and its dependence on the glass content of the shard.

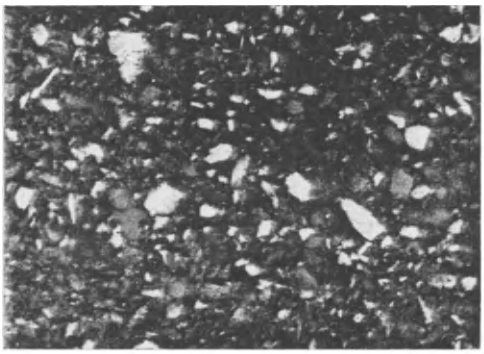


Fig. B 12-35 B II Porcelain: thin section (from VÚEK), mag. × 100

The same object as seen in Fig. B 12-35 B I but taken by transmitted polarized light; white grains are undissolved quartz fragments, the grey regions are glass phase (fused feldspar)

Fig. B 12-35C Fine-grain porcelain: thin section, ordinary transmitted light (from VÚEK), mag. × 100

White grains are quartz, at whose edges glass phase material can be easily seen (see also Fig. B 12-35D); black spots are pores; the rest of the shard is fine-grained with partial mullite formation

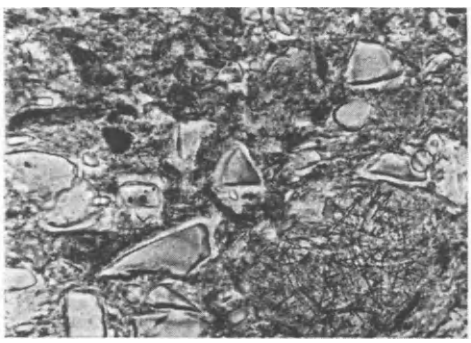


Fig. B 12-35D Porcelain: thin section taken by ordinary transmitted light (from VÚEK), mag. × 400

Large grains are quartz fragments surrounded by a glassy flux, produced from feldspar and melting of quartz grains. In the right lower part of the picture mullite formation, in the shape of fine needles, is clearly visible; the needles are about 50 μ long and 5 μ in diameter

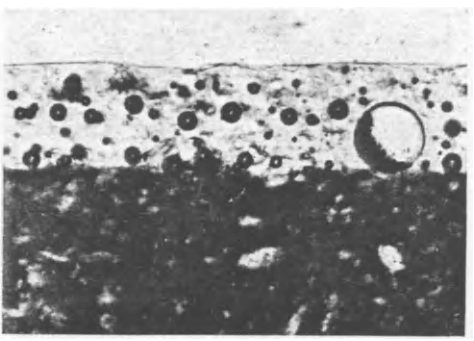


Fig. B 12-35E Thin cross-section of white (feldspar) glaze on a porcelain, taken by partly polarized transmitted light (from VÚEK), mag. × 125

Bubbles can be clearly seen in the glaze, in particular a large one at the right of the picture

The electrical properties also are strongly dependent on the content of base glass in the porcelain. Soda feldspar porcelains exhibit electrolytic effects to a more marked degree than potash feldspar types because of the higher Na-ion mobility (cf. also 10.1.XI). This electrolysis can also be detected at high temperature, under application

[12.3]

of D.C., by diffusion of foreign ions (e.g. Ag ions from fired-on Ag coatings) and by polarization currents (see, e.g., PFESTORF, SCHAUDINN). Compared with other types of ceramics, ϱ of feldspar porcelain is low at elevated temperatures but nevertheless

TABLE T 12–14. HYDROGEN PERMEABILITY OF CERAMIC TUBES
(I.D. 3 mm, LENGTH OF HEATED ZONE 180 mm, PRESSURE DIFFERENTIAL 300 Torr; cf. BAUKLOH)

[12.3]

TEMPERATURE °C	PERMEABILITY (cm³ (NTP)/hr)			
	UNGLAZED PORCELAIN 0.11 mm WALL	GLAZED PORCELAIN 0.15 mm WALL	K MATERIAL[1] 16 mm	SINTERED CORUNDUM[2], 1.6 mm
22	0.00	0.00	0.00	23.5
500	0.27	0.31	0.86	18.2
1000	0.33	0.23	1.18	–
1100	0.37	0.30	0.83	10.27
1200	0.33	0.36	1.07	–
1300	0.43	0.33	0.92	–

(1) Made by STAATLICHE PORZELLAN MANUFAKTUR DIN Type 610 (Table T 12–11 D); high-alumina ceramic with little glass phase.

(2) DIN Type 710 (Table T 12–11 D), virtually pure sintered alumina without glass phase.

higher than that of ordinary soda-lime glass (see Figs. B 12-18 and B 12-18 A). Figure B 12-20 shows the surface resistance of porcelain. The high content of alkali constituents is also the main cause of the high dielectric losses in porcelain (cf. Tables T 12–11 and T 12–15). Losses can be so high that a porcelain insulator at H.F. (especially at UHF) will be strongly heated and the thermal breakdown type of electrical rupture will ensue.

TABLE T 12–15. DIELECTRIC CONSTANT ε AND LOSS ANGLE $\tan\delta$ OF PORCELAIN AND ITS CONSTITUENTS AT 10^{10} c/s AND ROOM TEMPERATURE

MATERIAL	ε	$\tan\delta$ (10^{-4})
Feldspar (orthoclase), crystalized	4.70	52
fused	6.63	260
Fused silica	3.81–3.86	3.5–5
Alumina (corundum), crystalized	11–11.3	1.8–2.1
Ordinary electrical porcelain (25% feldspar, 25% quartzite, 50% kaolin)	5.3	200

Dielectric loss can be cut down by reduction in alkali content, but the necessary firing temperature becomes undesirably high and breakdown strength decreases. All this plus the fact that very large components can be made of porcelain, because the raw mass can be easily worked, are reasons why porcelain has become the most widely used ceramic for normal mains-frequency insulators (e.g. for tank rectifiers), both for high and low voltages, and above all in moist atmosphere locations and outdoors.

12.3.II. *Natural Rocks: Soapstone and Pyrophyllite*

There are naturally occurring lump minerals, Mg or Al silicates, of such purity and quality that they require no comminution and mixing with plasticizers, but can be machined (turned, etc.) and made into ceramic bodies after heating to a sufficiently high temperature. In the USA, ceramics made from natural rock are called "Lava" (see, e.g., Table T 12–10, A1: Lava Grade A made from Al-silicate, and Lava 1136 of Mg-silicate, both marketed by the AMERICAN LAVA CORP.).

The most important of these rocks is soapstone, a solid, compact cryptocrystalline *magnesium* hydrosilicate, originally found in the Fichtel Mountains but recently also in [12.3] the USA, Egypt, the Urals, Manchuria, etc. The Mohs' hardness is about 1, so that it can be easily worked with ordinary tools. However, the pieces suitable for working must be free of inclusions that can lead to melting, discoloration or fracture in subsequent firing, although in fact the material generally has a yellowish-green color due to its Fe_2O_3 content (*ca.* 1.6%). On heating, soapstone loses its chemibonded water in the range near 800°, the crystal lattice converts to crystalline enstatite and at higher temperatures to clinoenstatite. After working up, the material is fired at 1000–1400° depending on desired porosity; it densifies and the Mohs' hardness rises from 1 to 6–7. Since firing shrinkage is relatively low (1–3%), close tolerances can be held (EAGLE). Fired material has remarkable properties when compared with other ceramics, so is well-suited to making small numbers of piece-parts (e.g. models) where the cost of complex molds and tools would not be justified.

Table T 12–16 surveys the properties of fired soapstone, standardized under the old DIN Standard 40685 (1950) under type number 230. Soapstone can also be obtained commercially in the partly (pre-)sintered porous condition, which ensures good workability with the aid of ordinary steel tools; it must then be fired again at 1400°, the shrinkage being less than 1%. Table T 12–11, A1, nos. 26 and 27, contain data on commercial ready-fired ceramics made from natural Mg-silicate (Lava 1136 and 1137).

There is another natural rock directly usable for the production of ceramic piece-parts; this material occurs in the Transvaal, South Africa, and in Russia (Bielorussian SSR), the lumps being larger than usual for soapstone. The material is called pyrophyllite, G-stone, Koranna stone or Wonder-stone (see, e.g., HYDE). It is an *aluminium* silicate ($3–4\ SiO_2 \cdot Al_2O_3 \cdot H_2O$) with the approximate composition 54–75% SiO_2, 20–34% Al_2O_3, up to 2.5% TiO_2 and up to 2% ($Fe_2O_3 + CaO + MgO$). It can be easily worked before firing, and can be fired at about 1435° with only 3–4% shrinkage; after firing it consists chiefly of quartz, alumina and mullite. The main properties are collected in Table T 12–16. They are similar to those of fired soapstone with the exception of the much smaller α, higher dielectric loss, and, at elevated temperatures, an insulation resistance less by about an order of magnitude. Data on commercial ceramics made from natural Al-silicate are to be found in Table T 12–11, A1, no. 25 (Lava Grade A).

The use of naturally occurring ceramics—especially for making small insulators in tube electrode mounts—has decreased considerably since degassable ceramics of forsterite or steatite have been successfully made, which can be satisfactorily machined in the fired state with ordinary tools; examples of such porous ceramics are Ergan (Germany), Porolit (Czechoslovakia), and Alsimag 222 (USA). See Tables T 12–10 and T 12–11 D and A1, also 12.3.III*b*.

TABLE T 12-16. PROPERTIES OF FIRED SOAPSTONE AND PYROPHYLLITE (OLD DIN STANDARD 40 685/5.50, AND [1,2]THURNAUER)

		SOAPSTONE	PYROPHYLLITE (TRANSVAAL)
Water take-up	%	≈ 3	1–3
Apparent density	g/cm³	2.6–2.8	2.3
Refractoriness	°C	1500	≈ 1400
T_{soft}	°C	980–1100	1200
[12.3] Tensile strength	kg/mm²	≈ 1.75	1.75
Compressive strength	kg/mm²	14–21 40–80(4)	≈ 14
Bend strength	kg/mm²	6.4 (≈ 10)(4)	4.9–6.3
Impact bend strength	kg · cm / cm²	0.4–6	≈ 7(3)
Young's modulus	kg/mm²		28,000–30,000
Mohs' hardness		6–7	6
Thermal expansion coeff. (20–700 °C)	10^{-7} / °C	≈ 115 20–100 °C: 90–400(4)	36
Thermal shock resistance	°C	≈ 100	200–220(1)
Thermal conductivity	cal / cm s °C	≈ 0.005	0.003–0.005
Elec. breakdown strength	kV/cm	≈ 40	≈ 32(2)
Electrical resistivity	Ω-cm	200 °C ≈ 10^{11} 300 °C ≈ 10^{10} 400 °C ≈ 10^{8} 500 °C ≈ 10^{8}–10^{7} 600 °C ≈ 10^{7} 800 °C ≈ 10^{6} 1000 °C ≈ 10^{5}	20 °C : 10^{12}–10^{15} (Te-Value = 600–900 °C)
Dielectric constant (10^6 c/s)	–	≈ 6 (5.8)	5–6
Loss angle tan δ (10^6 c/s)	10^{-4}	3–10 20–30(4)	≈ 100×10^{-4}

(1) Measured on rods 25 mm dia., 25 mm long.
(2) Measured on plates 6 mm thick.
(3) Measured on rods 12.5 mm dia.
(4) According to STEMAG 1941.

12.3.III. *Magnesium-Aluminium-Silicates*

Special ceramics most used in vacuum technology belong to the ternary system magnesia-alumina-silica, $MgO–Al_2O_3–SiO_2$, often increased to a quarternary system by an alkali or alkali earth component. The phase diagram is given in Fig. B 12-36. Names for the various regions in the diagram refer to the crystal that predominates when the melt of that composition is cooled and—since in firing many components begin to melt—the crystals therefore expected in the ready-fired ceramic. When preparing the starting material, MgO, if not already effective as a component of talc or soapstone used in the mix, is incorporated as the carbonate (magnesite), hydroxide (brucite) or

even as the oxide. Alumina can be introduced as kaolite (Al-hydrosilicate), sillimanite ($Al_2O_3 \cdot SiO_2$) or mullite ($3\,Al_2O_3 \cdot 2\,SiO_2$), or even as corundum ($Al_2O_3$). SiO_2 is mostly used in the form of quartz sand (flint) or even as ground rock quartzite.

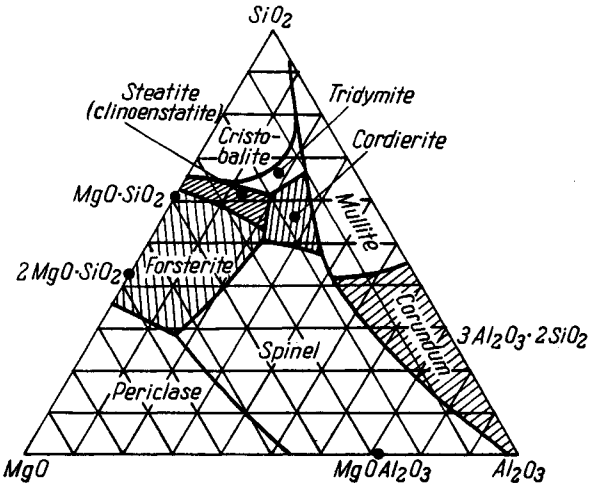


Fig. B 12-36 Phase diagram of the ternary system MgO–Al_2O_3–SiO_2

The names of the zones are those of the chief crystals which form on cooling a ceramic melt of given composition. The most important regions for technical silicate ceramics, which may also contain alkali or alkali earth oxides, are indicated by hatching

[12.3]

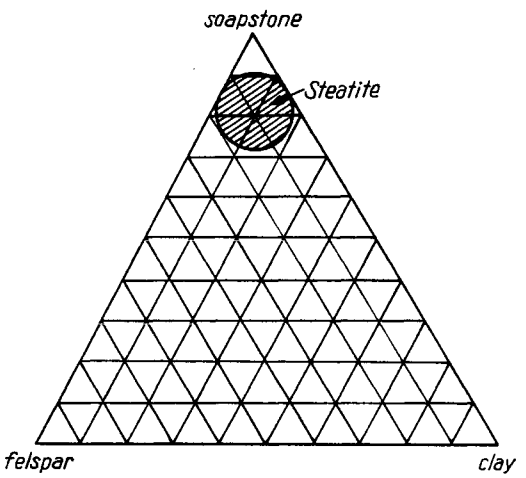


Fig. B 12-37 Composition of steatites in the ternary soapstone-clay-feldspar system

12.3.III*a*. *Steatite* (GUNZENHAUSER, HAUSER, PALATZKY, SALMANG, [3]THURNAUER).

The realization that soapstone (steatite) or talc converts on heating to a material with the properties of a good ceramic has led to the use of milled soapstone or talc as starting materials for ceramics. Soapstone is fine-crystalline, has no coarse structure and is yellowish-green; talc is fibrous or flaky, and types with less than 0.5% Fe_2O_3 are pure white.

As binder and aid to sintering, small amounts of clays and potassic feldspar or BaO (as $BaCO_3$) have to be added. Typical starting batches would consist of about 70–87% steatite (soapstone or talc), 7–15% clay and up to 10% feldspar (see Fig. B 12-37). The ceramic, which after firing contains clinoenstatite, is called a steatite. Its position in the ternary system is made clear by Fig. B 12-36. Talc or soapstone content has a characteristic unctuous quality and, after the steatite has been fine-milled, this quality facilitates manufacture of *dry*-pressed bodies which therefore have low shrinkage; another consequence is that very sharp-edged moldings can be made. This process
[12.3] requires expensive chrome-steel molds, but they can be used in automatic machines (Fig. B 12-6A) for mass-production. The sintering range, which generally lies between 1300° and 1400° according to the batch, is relatively short for steatite and in normal cases amounts to about 30–40°, and for many low-loss steatites only 10–20°; compare

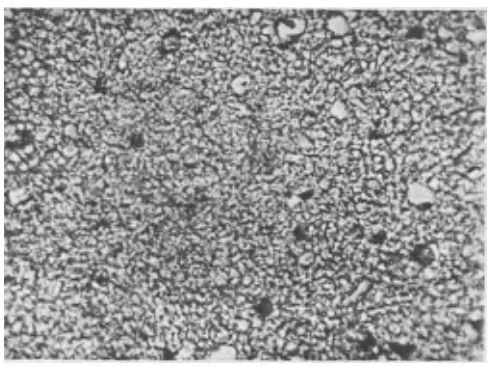


Fig. B 12-37A Steatite (Calit) thin microsection taken by ordinary transmitted light (VÚEK), mag. × 300

Larger bright zones = empty pores; larger dark zones = pores with trapped grinding agent; rest is fine-grained structure with insignificant amount of glassy phase at the grain boundaries

porcelain with a range of 50–90°. This means that very precise temperature control is required in firing. Firing shrinkage for dry-molded pieces is only about 8–11% so that linear tolerances of 0.5–2% can be easily held, and this can be cut to $\pm 15\,\mu$ by finish-grinding.

Dense-fired steatites have a pore-free structure in which, as stated, one can observe mainly clinoenstatite crystals with a small amount of crystobalite plus a little glass-phase material (Fig. B 12-37A). The latter arises from the reaction between the flux (feldspar or BaO) with Mg-silicate during firing. This homogeneous crystalline structure primarily gives rise to the high mechanical strength of steatites, and the very low alkali content is the chief cause of its superior electrical qualities by comparison with porcelain; this material has an unhomogeneous, fine structure of mullite and quartz crystals, and a high feldspar glass (alkali) content, leading to higher conductivity and dielectric losses. The superiority of steatite over porcelain is best seen by the comparison given in Table T 12–17 (cols. 2 and 3), even though this table can only give average values because of the large number of special steatite ceramics. Ordinary steatites have $\tan\delta$ values only one-tenth of those of porcelains, but besides the electrical improvements, the mechanical strength values are the most striking. αs of steatites are larger than those of porcelains, and lie in the range of medium-hard and soft technical glasses and their (iron) sealing alloys (see 6.1).

TABLE T 12-17. COMPARISON OF THE MOST IMPORTANT (AVERAGE) PROPERTIES OF HARD PORCELAINS AND MgAl CERAMICS (RADIO INDUSTRY COUNCIL, SEE ALSO [1]THURNAUER)

1 PROPERTY			2 HARD PORCELAIN	3 STEATITE	4 FORSTERITE	5 HIGH-ALUMINA CERAMICS
Density		g/cm³	2.3–2.5	2.5–2.8	2.8–3.1	3.4–3.5
Max. operating temp.		°C	1000	1000	1000	1350
Tensile strength		kg/mm²	2.8–5	5–10	7	20
Compressive strength		kg/mm²	35–55	50–100	60	210
Bend strength		kg/mm²	4–10	11–17	14	32
Impact bend strength		$\frac{\text{kg cm}}{\text{cm}^2}$	1.7–2.2	3.7–5	4.3	6.5–8.6
Young's modulus		kg/mm²	4900–9800	9100–12,600	–	23,800 to 38,500
Mohs' hardness			7–8	7.5	7.5	9
Lin. thermal expansion coeff.	25–100 °C	10⁻⁷/°C	30–60	60–80	≈ 90	40–60
	25–700 °C	10⁻⁷/°C	50–70	80–90	100–110	60–90
Thermal conductivity		$\frac{\text{cal}}{\text{cm s °C}}$	0.003–0.004	0.006	0.008	0.020
Elec. rupture strength (50 c/s)		kV/cm	100–380	350–450	300–450	100–500
Electrical resistivity (50 c/s)	20 °C	Ω-cm	$> 10^{14}$	$> 10^{14}$	$> 10^{14}$	$> 10^{14}$
	300 °C	Ω-cm	10^{7}	10^{10}–10^{11}	10^{11}–10^{12}	10^{8}–10^{9}
	600 °C	Ω-cm	10^{4}–10^{5}	10^{7}	10^{9}	10^{5}–10^{6}
	900 °C	Ω-cm	10^{3}	10^{5}–10^{6}	10^{6}–10^{7}	10^{4}
Te value (10^{6} Ω-cm)		°C	450	820	> 1000	600–700
Dielectric constant ε		–	5–7	5.5–6.5	6.2–6.4	8–10
Loss angle $\tan\delta$ at 1 Mc/s, 20 °C		10^{-4}	60–120	3–5	≈ 2	6–40

[12.3]

A further reduction in dielectric loss of steatite can be achieved with so-called "special steatites", in particular by use of soapstones and talcs with very small crystallites and with low iron oxide content, by reduction of alkali content and use of additives like alkali earth carbonates and BaO. This results in materials which have the same possibilities for making moldings as before, and with $\varepsilon \cdot \tan\delta$ values, in the H.F. range at least, almost as low as those of mica and quartz, although in the L.F. range, and often at elevated temperatures, they are larger (see, e.g., Figs. B 12-31 and B 12-32). The starting batch for these low-loss steatites, which are generally fired at 1300–1400°, has an average composition of 65–87% steatite, 4–13% clay and 7–15% alkali earth carbonates. Table T 12–18 gives a special example of the composition of the starting batch and the firing data for a type of the well-known steatite "Frequenta". Analyses of fired low-loss steatites gives the following approximate values:

SiO_2	MgO	Al_2O_3	BaO	K_2O	Na_2O
54–59	27–28	3.5–7.5	5.5–7.5	0.15–0.45	0.03–0.15 w/o

Addition of alkali earths facilitates formation of a glass phase which penetrates the crystalline structure, closes remaining pores or gaps, and thus enhances the vacuum-tightness of the ceramic.

By employing low firing temperatures, *porous* low-loss ceramics can be produced such as are used for distance pieces, in tube electrode systems (see 12.5.V).

TABLE T 12–18. STARTING MATERIALS, FIRING DATA, AND CHARACTERISTIC DIELECTRIC PROPERTIES OF A SPECIAL STEATITE (FREQUENTA AS 42a) (FROM [1]SNYDER)

[12.3]

Starting batch:		
Göpfersgrüner Steatite	%	87
Wildsteiner blue clay	%	4
Barium carbonate	%	8
Calcite	%	1
Milling time, wet (500 kg mill)	hr	20
Sieve residue (6400 mesh/cm^2)	%	2.8
Firing temperature	°C	1270–1280
Firing time	hr	1
Dielectric constant	ε	*ca.* 6
Loss angle	$\tan\delta$	*ca.* 5×10^{-4}

12.3.III*b*. *Forsterite*

If the MgO content of quality steatite batches is increased by the addition of $MgCO_3$ or synthetic MgO, the finished product develops partly or wholly the compound called forsterite ($2\,MgO \cdot SiO_2$), in place of the crystal compound of ordinary steatite, clinoenstatite ($MgO \cdot SiO_2$). Because of the dominating influence of the material formed, such a ceramic is called forsterite (cf. Fig. B 12-36). These ceramics are of recent date. They were developed not only because their $\tan\delta$ values are less than those of steatites even at UHF (see Table T 12–11, A1, no. 13 and D γ, no. 4) but also because of demands in vacuum technology for really vacuum-tight ceramic with a thermal expansion that permits hard-soldered joints to the well-known FeNi alloys (see, e.g., ELLEFSON, and Chapter 32).

In addition, the manufacturing process for forsterites offers certain advantages as compared with steatites, mainly the long firing range or interval. Figure B 12-37B shows thin sections of a European forsterite ceramic. Table T 12–19 gives an example of the compositions of the starting batch and raw materials, and the firing temperature of an American forsterite; Fig. B 12-38 shows the expansion characteristic of this material in comparison with forsterite "Alsimag 243" and a FeNi sealing alloy, while Fig. B 12-39 shows the curve of electrical resistivity as a function of temperature for this forsterite, from which the superior insulation properties even at elevated temperatures can be seen. Commercial forsterite "Alsimag 243" is vacuum-tight from thicknesses of 0.5 mm up.

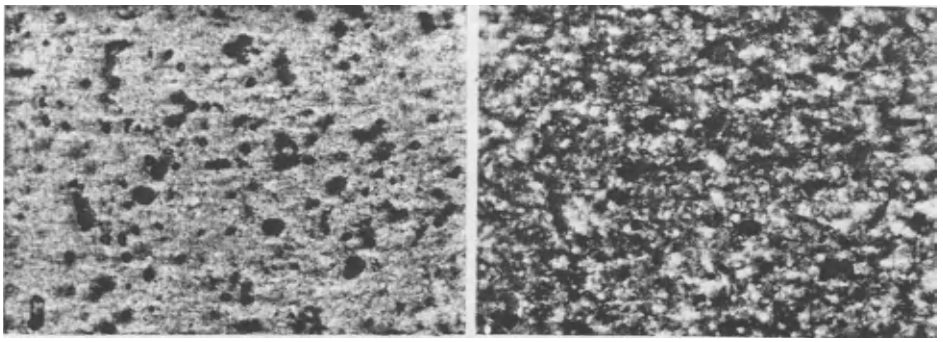
TABLE T 12-19. COMPOSITION AND SOME CHARACTERISTIC DATA OF A VACUUM-TIGHT FORSTERITE "189-2 C" ([2]NAVIAS)

1	Composition of starting batch	w/o	Talc[1] 55 $Mg(OH)_2$ 33 $BaCO_3$[4] 6.4 Clay 3.6	ANALYSES See no. 2 – See no. 3 See no. 4
2	Analysis of raws: Sieramic talc	w/o	SiO_2 59.62 MgO 29.91 Al_2O_3 2.05 Fe_2O_3 0.94 CaO 0.91 $K_2O + Na_2O$ 0.49 Loss in firing 5.98	[12.3]
3	$BaCO_3$	w/o	BaO 77.6	
4	Clay: Kentucky ball-clay no. 4	w/o	SiO_2 51.65 Al_2O_3 31.24 MgO 0.50 K_2O 0.36 Na_2O 0.58 CaO 0.20 TiO_2 1.72 Fe_2O_3 1.17 Loss in firing 12.13	
5	Firing temperature to vacuum-tightness	°C	1275–1325	
6	Analysis of finished ceramic	w/o	SiO_2 40 MgO 48 Al_2O_3 3 BaO 6 rest (TiO_2, CaO, Fe_2O_3, Na_2O, K_2O) *ca.* 3	
7	Bend strength	kg/mm^2	8.3	
8	Expansion coefficient 25–300° 25–400° 25–500°	 10^{-7}/°C 10^{-7}/°C 10^{-7}/°C	 101.7 104.4 105.7 } see also Fig. B 12-38	
9	Electrical resistivity	Ω-cm	cf. Fig. B 12-39	
10	*Te* value	°C	*ca.* 1100	
11	Dielectric constant ε	–	At 10^{10} c/s: 6.27	
12	Loss angle tan δ	10^{-4}	At 10^{10} c/s: 6	

The relatively high α of forsterite unfortunately results in a rather low thermal shock resistance (cf. Table T 12–6) that often makes its use in particular cases questionable.

Besides dense forsterite, there are also porous forsterites of similar structure whose primary use is electron-tube mount insulators, and which have the advantage that

[12.3]



I II

Fig. B 12-37B Forsterite; thin microsection, mag. × 500 (VÚEK)

I taken by ordinary transmitted light: dark zones = pores; shard has fine crystal structure
II same object taken by transmitted polarized light

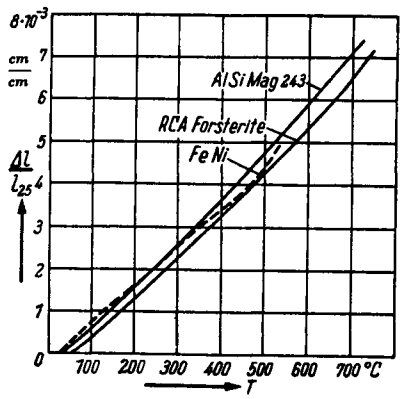


Fig. B 12-38 Expansion curve of RCA forsterite and Alsimag 243 forsterite, compared with a FeNi sealing alloy (PRYSLAK, see also [4]THURNAUER)

The curve for RCA material is shifted to the right by 25° to make the diagram clearer

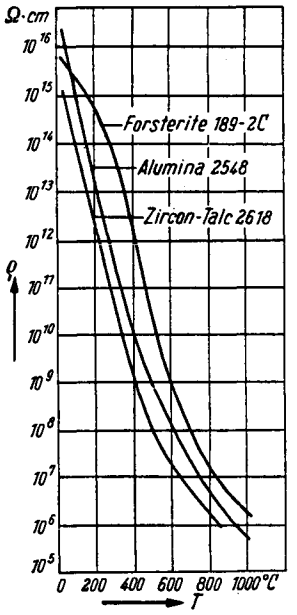
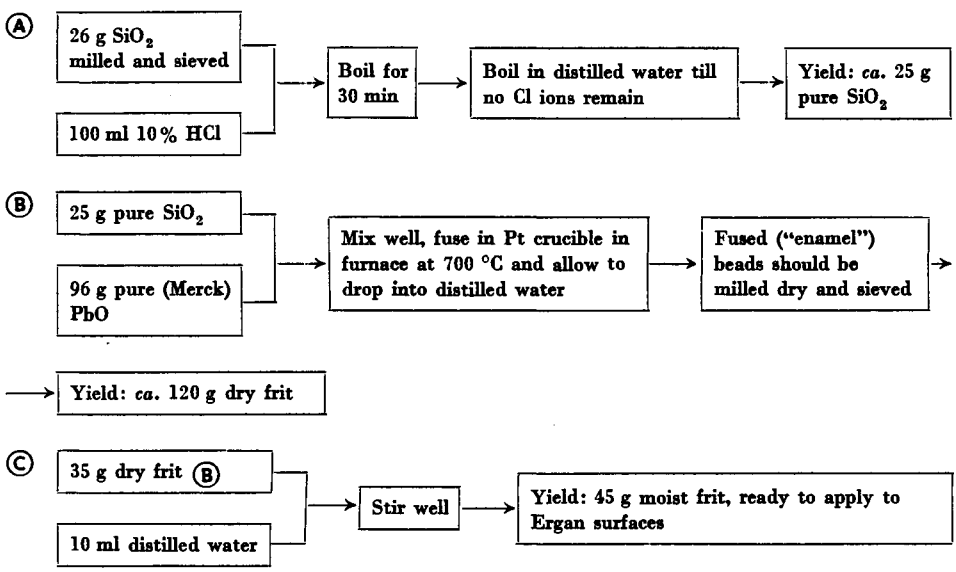


Fig. B 12-39 Electrical resistivity ϱ of types of ceramic specially suited to making ceramic-metal joints ([2]NAVIAS)

they can be machined in the fired state, without grinding, by carbide tools and with about the same cutting speed as for machining iron. This stems from the weak bonding in a porous ground mass of particles that themselves are very hard to machine. The first such forsterite material was marketed under the name of "Ergan" ([3]ALBERS-

SCHÖNBERG), made essentially from 14% clay, 8% talc and 78% orthosilicate, fired at 1200–1300°, and had the final composition: 47% MgO, 9% Al_2O_3, 44% SiO_2. However, similar properties can be achieved with porous enstatite bodies such as Alsimag 222 (Tables T 12–10, and T 12–11, A 1) or Porolite (Table T 12–11 c). Ergan differs from ordinary steatites, which are made by use only of *naturally-occurring* silicates, since it is prepared from very pure *synthetic* oxides and oxide mixtures, finely-milled and made fictile by small additions of plasticizer. It can be turned by steel tools of the usual shape and a feed of up to 0.2 mm per rev. is acceptable. The depth of cut (with a feed of 0.1 mm per rev.) can amount in exceptional cases to 3 mm. It is best to drill with a [12.3] pointed tool with carbide insert, on a wood drill-bed. By using a good support, one can avoid break-out of the edge of the hole when the drill comes through. Milling, countersinking and circle-cutting are also done with carbide tools. It is relatively easy to cut threads; to save wear on the tool it is recommended that the cutting speed be not too

TABLE T 12–19 A. FRIT FOR JOINING ERGAN PLATES


Ⓐ
26 g SiO_2 milled and sieved
100 ml 10% HCl
Boil for 30 min
Boil in distilled water till no Cl ions remain
Yield: *ca.* 25 g pure SiO_2
Ⓑ
25 g pure SiO_2
96 g pure (Merck) PbO
Mix well, fuse in Pt crucible in furnace at 700 °C and allow to drop into distilled water
Fused ("enamel") beads should be milled dry and sieved
Yield: *ca.* 120 g dry frit
Ⓒ
35 g dry frit Ⓑ
10 ml distilled water
Stir well
Yield: 45 g moist frit, ready to apply to Ergan surfaces

high. It is an indication of the relatively good mechanica lstrength of Ergan that, in spite of porosity, metal screws can be tightened down quite well in such threads (see also Table T 12–11, D β, type 240). Sheet or bar is most effectively sawn up with grinding wheels 2 mm thick; round rod can be parted off with carbides such as Widia steel. Filing should be avoided ([2]ALBERS-SCHÖNBERG). Ergan components can be satisfactorily joined with a solder glass (Table T 12–19 A); they are laid together along a straight edge with an interlayer of the glass powder, possibly under light pressure, and then heated to 800–1000°. The glaze melts and cements the parts to a strong unit without warping. Ergan has, like forsterite, very low dielectric loss at H.F. ($\tan\delta = 2\text{–}4 \times 10^{-4}$, $\varepsilon = 4.5$ approx., both at 10^6 c/s).

12.3.III*c*. *Cordierite*

If the ternary system $MgO–Al_2O–_3SiO_2$ is chosen to have a composition of about 8–14% MgO, 30–35% Al_2O_3 and 55–60% SiO_2 (see Fig. B 12–36), a low expansion type of ceramic (Table T 12–5) is obtained, which will therefore have a high thermal shock resistance; refer to Table T 12–6. The basis of the low α is the cordierite crystal content ($2\ MgO \cdot 2\ Al_2O_3 \cdot 5\ SiO_2$) which gives its name to the ceramic. An example of the composition of a starting batch for porous cordierite is: 40% talc, 40% plastic clay and 40% grog. An example of a make-up batch for a 60% cordierite crystal ceramic to be [12.3] dense-sintered at 1380–1410°, would be: 30% talc, 38% plastic clay, 17% grog *plus* 7% feldspar (BUDNIKOW). Otherwise, the manufacture of cordierite is like that of porcelain because of the high content of plastic clay; it is made more difficult by the very short sintering range. By adding small amounts of feldspar the sintering range can be expanded to an acceptable value.

Both porous and dense-fired cordierites have excellent thermal shock resistances as mentioned above, and are therefore chiefly used for insulators exposed to sudden temperature changes (such as at the striking of an electric arc). The dielectric loss of cordierites is lower than that of porcelain, but always higher than that of steatite or forsterite ceramics. The mechanical strengths roughly correspond to those of unglazed porcelain.

12.3.III*d*. *Alkali-free aluminium silicates* (HYNES, [2]SNYDER)

For vacuum work, and especially at H.F., the chief materials are the alumina-rich bodies of the $SiO_2–Al_2O_3$ system, with a small content of a suitable mineralizer such as MgO, which lie in the $MgO–Al_2O_3–SiO_2$ system (Fig. B 12-36) between mullites (alumina content less than 72%) and pure alumina. For Al_2O_3, or sintered corundum, see 12.6.I. They are generally made from sillimanite, kaolin, alumina (clay), synthetic alumina (corundum), quartz or quartz sand. Sillimanite, i.e. $Al_2O_3 \cdot SiO_2$, decomposes at firing temperatures of 1300–1750° to mullite and quartz:

$$3\ (Al_2O_3 \cdot SiO_2) = 3\ Al_2O_3 \cdot 2\ SiO_2 + SiO_2.$$

Nevertheless, ceramics produced from sillimanite as a constituent are often called "sillimanite ceramics". As a rule a ceramic only takes on the name "high-alumina" when it contains more Al_2O_3 than is needed for mullite formation. Mullite = $3\ Al_2O_3 \cdot 2\ SiO_2$ = 71.8 w/o Al_2O_3 + 28.2% SiO_2. Refer to Fig. B 12-39A on this point.

The firing temperatures for high-alumina ceramics are around 1400–1800°; the value chosen is higher the lower the SiO_2 (glass phase) content, which, however, contributes to gas-tightness. For this reason, and to lower the sintering temperature, small amounts of flux containing silicates are added to the batch (e.g. clay or talc additions), but the alkali content must be kept as small as possible in the interests of high insulation resistance even at elevated temperatures.

Batches are best milled in high-alumina material to avoid entrainment of SiO_2 and other impurities from the mill lining. The batch is mostly milled down to 2–10 μ grain size. The most important point to watch is freedom of the batch from Fe (magnetic separator and HCl rinsing required), and also from TiO_2 which even in amounts as

small as 0.25% will discolor the ceramic when heated in a reducing atmosphere (e.g. when hard-soldering) and can also lead to deterioration of dielectric properties. This is quite apart from the fact that TiO_2 favors formation of a coarse crystalline structure. The material can be formed by extrusion, but is mostly dry-molded and cast (some binder may be added). The batch particles are very hard so that dies with a hard-chromed surface, or in the case of simple shapes, carbides such as Widia or Diadur, are necessary. Recently use has been made of "isostatic molding", a process in which a flexible mold (e.g. rubber) is filled with powdered material and exposed to very high hydrostatic pressure on all sides (Fig. B 12-68A). [12.3]

Firing is usually carried out in tunnel furnaces on a floor of fused alumina sand; the sintering range is not inconveniently short. The temperatures needed vary from 1400° to 1800° according to alumina content (75–100%). Figure B 12-39B shows micrographs

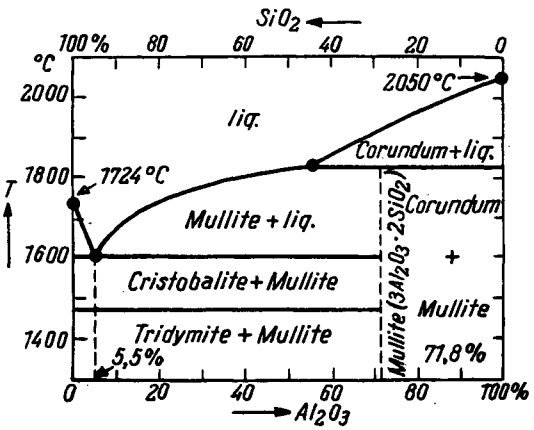


Fig. B 12-39A The phase diagram for the binary Al_2O_3–SiO_2 system (BOWEN, LUKS)

of ceramics (85–99% alumina) taken with an optical and with an electron microscope. Standard values for the main properties of high-alumina ceramics are given in column 5 of Table T 12–17 and of ceramics with various alumina contents in Table T 12–19B. Table T 12–11, A1 contains values for commercial high aluminas with various alumina contents, under numbers 14, 19, 21–24.

Table T 12–20 contains data for an *American* silicate ceramic, sintered to vacuum-tightness: composition of starting batch and the raw materials used to make it, firing temperature and main properties. Table T 12–20A gives a complete production schedule for a *European* corundum ceramic which was developed mainly from the viewpoint of high mechanical strength and thermal conductivity (automobile spark-plug ceramic). Finally, Table T 12–21 consists of analyses of some commercial finish-fired alumosilicate ceramics.

The chief advantage of alumosilicates lies in their refractoriness, which exceeds that of all other silicate ceramics, their outstanding mechanical strength and, in the sintered state, high thermal conductivity (see for comparison Table T 12–17). Expansion coefficient rises with alumina content and runs between 70 and 80×10^{-7}/°C (Fig. B 12-40). The high content of crystalline corundum gives the material great hardness (9 on Mohs'

TABLE T 12-19 B. PROPERTIES OF HIGH-ALUMINA CERAMICS WITH VARIOUS Al_2O_3 CONTENTS (³ANON.)[1]

								REFER TO FIGS.
Al_2O_3 content		w/o	85%	95%[2]	99.5%	99.5%	100%[3]	
Structure		–	Dense	Dense	Dense	Porous	Dense	
Density		g/cm³	3.40–3.53	3.61–3.75	3.7 (–3.97)	2.4–3.4	3.79–3.87	
Porosity		%	< 1[4]	< 1[4]	< 1	7.2[5]		
Water absorption		%	0.00–0.02	0.00	0.00	7–1.8		
Mohs' hardness		–	8.5–9	9	9	–		
Max. working temp. (T_{work})		°C	1300–1400	1600–1700	1950	1400–1800	1800	B 12-69
Tensile strength		kg/mm²	12–16	17.5–24.5	26.3–27	–	26.5	B 12-62, B 12-62 A, B 12-62 B
Compressive strength		kg/mm²	98–280	175–280	300	7–87	300	B 12-63
Bend strength		kg/mm²	21–32	32–35	30–33	7–15	33	
Young's modulus		kg/mm²	21,700–24,500	27,300–30,000 [6]	36,400	–	34,800–38,500	B 12-60 B
Specific heat		$\frac{cal}{g\ °C}$	0.18	0.188–0.190	0.22	–	0.26 (1000 °C)	
Thermal conductivity	100 °C	10^{-3} cal	31–40	45–52	47	40	47–90	B 12-65
	870 °C	cm s °C	(79)	(107)	–	–	≈ 12 (1000 °C)	B 12-65 A
Thermal expansion coeff.	25–200 °C	10^{-7}/°C	54–57	57–67	–	51	(54)	B 12-14
	25–700 °C	10^{-7}/°C	76–79	81	77	–	76	B 12-40
	25–1000 °C	10^{-7}/°C	77–79	85–91	84	–	85	B 12-64
Electrical breakdown strength	25 °C	kV/cm	82–140	100–160	152	20	≈ 150	B 12-24
	500 °C	kV/cm	–	40–48	–	–	–	
	1000 °C	kV/cm	–	8–12	–	–	–	

Electrical resistivity	300 °C	Ω-cm	$(1–5)\times10^{10}$	5.3×10^{12}	1.2×10^{13}	$10^{10}–10^{11}$	$10^{12}–10^{13}$	B 12-18A
	500 °C	Ω-cm	$10^{8}–7.5\times10^{9}$	$(1.2–4.5)\times10^{10}$	1.3×10^{11}	$7.5\times10^{7}–10^{9}$	$2\times10^{10}–3\times10^{11}$	B 12-19
	700 °C	Ω-cm	3.7×10^{6}	6×10^{8}	–	3.6×10^{6} to 3.0×10^{7}	$3\times10^{8}–5\times10^{9}$	B 12-39
	900 °C	Ω-cm	4.5×10^{5}	–	–	5.6×10^{5}	$10^{7}–2\times10^{8}$	B 12-67
Te value (10^{6} Ω-cm)		°C	750–1000	800–1100	1100	835–1100	1000–1200	B 12-67
Dielectric constant ε	10^{6} c/s 25 °C	–	7.4–8.95	8.81–9.6	–	5.5	9.5–12	B 12-41
	10^{6} c/s 500 °C	–	8.87	9.03	–	–		
	10^{10} c/s 25 °C	–	8.08–8.77	8.4–9.36	–	7.07		
	10^{10} c/s 500 °C	–	8.26	9.03	–			
Dielectric loss angle tan δ	10^{6} c/s 25 °C	10^{-4}	7–12	2.5–3.5	–	5		B 12-29 (curve 6)
	10^{6} c/s 500 °C	10^{-4}	240	120	–	–		B 12-30 (curve 2)
	10^{10} c/s 25 °C	10^{-4}	27	8–15	–	–	$(5\times10^{7}$ c/s)	B 12-32 (curve 8)
							10–20	B 12-41
	10^{10} c/s 500 °C	10^{-4}	33	21	–	(1.1)		B 12-42

(1) Cf. also values for commercial ceramics with varying Al_2O_3 content as in this reference table.

Al_2O_3 content	85% (dense)	93% (porous)		96% (dense)	98% (dense)	>99% (porous)
Table T 12-11, A 1	No. 22	No. 14	No. 19	No. 23	No. 24	No. 21
Trade name	Alsimag 576	Alsimag 393 see also Table T 12-12	Alsimag 544	Alsimag 614	Alsimag 652	Alsimag 548

(2) Cf. also Table T 12-20.

(3) Cf. also Table T 12-26.

(4) Gas-tight, measured with He mass-spectrometer on 250 μ thick, ground disks.

(5) Pore dia. 2–3 μ.

(6) POISSON ratio *ca.* 0.25.

scale) and therefore grinding to tolerance can be carried out only with the help of wheels loaded with diamond dust. This plus the high firing temperature naturally makes

[12.3]

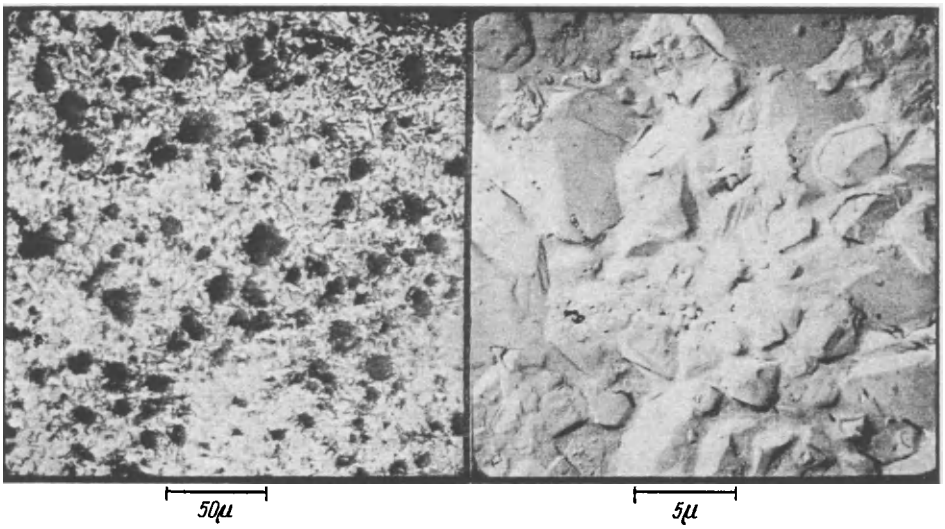


Fig. B 12-39B Aluminium silicate ceramic (85% Al_2O_3 present in form of corundum). Micrograph of polished surface. *Left:* mag. ×200 approx.; *right:* mag. ×5000 approx. ([2]RIGTERINK)

Considerable amounts of glass phase and pores can be seen as well as relatively fine Al_2O_3 crystals

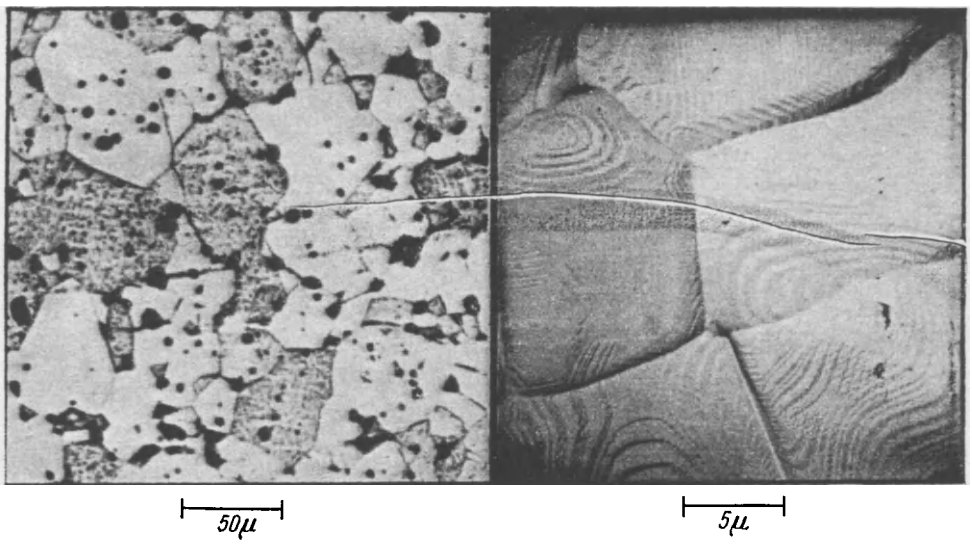


Fig. B 12-39C High-alumina ceramic (99% Al_2O_3). Micrograph of polished section. *Left:* mag. ×200 approx.; *right:* mag. ×5000 approx. ([2]RIGTERINK)

The Al_2O_3 crystals are much larger than in Fig. B 12-39B, the glass content is very low, and the pores are smaller; cf. Fig. B 12-68B

TABLE T 12–20. COMPOSITION AND SOME PROPERTIES OF A VACUUM-TIGHT HIGH-ALUMINA CERAMIC "2548" (²NAVIAS)

1	Composition of starting batch	w/o	Al_2O_3 95	For analysis see No. 2 below
		w/o	clay 2	See Table T 12–19, No. 4
		w/o	talc 3	see Table T 12–19, No. 2
2	Analysis of the Al_2O_3 (type Norton 38 900)	w/o	SiO_2 0.04	CaO –
			Fe_2O_3 0.01	MgO –
			Na_2O 0.05	Al_2O_3 (balance) 99.90 [12.3]
3	Firing temperature (in H_2 furnace)	°C	1775	
4	Density	g/cm³	3.5	
5	Bend strength	kg/mm²	17.5–21	
6	Expansion coeff. (25–500 °C)	10^{-7}/°C	*ca.* 78.5 (see also Fig. B 12-40)	
7	Electrical resistivity	Ω-cm	Cf. Fig. B 12-39	
8	*Te* value	°C	*ca.* 950	
9	Dielectric constant (10^{10} c/s)	–	8.2–8.6	
10	Dielectric loss angle tan δ			
	(10^6 c/s)	10^{-4}	*ca.* 4	
	(10^{10} c/s)	10^{-4}	5–8	

the cost of manufacture of high-alumina (corundum) ceramics very high. Dielectric losses are low even at elevated temperatures (cf., e.g., Fig. B 12-41), and in fact they are less the greater the Al_2O_3 content (Fig. B 12-42). Dense-sintered silicate ceramics

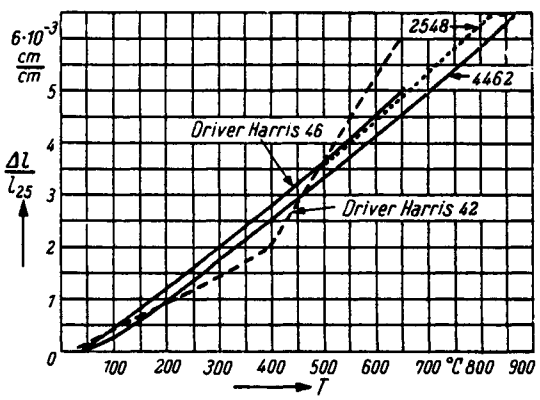


Fig. B 12-40 Expansion characteristic of alumina ceramics "2548" made by RCA and Almanox 4462 made by the FRENCHTOWN PORCELAIN CO., compared with two FeNi sealing alloys Driver Harris 46 and 42 (which see in Table T 6.1–2 and Fig. B 6.1-3B) (BURNSIDE, ²NAVIAS); see also Fig. B 12-14

containing alumina are exceptionally vacuum-tight even when there is little glass phase present; this has been shown by He mass-spectrometer tests on disks ground to 0.25 mm thickness (HYNES). On the other hand, highly-porous aluminas like Alsimag 393 are readily degassed because of their low glass-phase content and few closed pores.

TABLE T 12-20A. PRODUCTION SCHEDULE FOR A HIGH-ALUMINA CERAMIC OF BOSCH, STUTTGART (FROM [2]SNYDER)

I *Preparation of the* Al_2O_3

Pure synthetic Al_2O_3 is ball-milled, sieved through 27,000 mesh/cm^2 screening, given a sedimentation sizing-test, washed in HCl + steam to remove Fe, washed off 6 or 7 times in distilled water till latter is neutral, dried in Al vessels at 105–110 °C, milled again in ball-mill with special soft-rubber lining (see 12.6.I).

II *Preparation of the kaolin* (China clay)

[12.3]

Zettlitzer kaolin is washed, dried, powdered	(66.7)%	Tbese two percentages make up kaolin mix II, which serves as a flux and reduces sintering temperature
Seilitzer kaolin is pre-fired at 1450 °C to remove impurities and reduce shrinkage	(33.3)%	

III *Composition of the additive*

Powdered lime, dried	8.1%	Additive and binder III
Powdered MgO	8.6%	
Powdered quartz	11.9%	
Kaolin mix II	71.4%	

IV *Batch*

Al_2O_3 powder, dried, prepared as per I above	82.13%	Total batch, well blunged with 9.5% distilled water, then granulated
Additive III	17.87%	

V *Processing*

Press 75–250 g at 500–1000 kg/cm^2
Dry at 320 °C for 30–90 hr
Firing process: heat relatively fast up to 1150 °C, then slowly to 1650°, then relatively rapidly to 800°, then slowly cool to room temp. Overall firing time 20–72 hr. Sbrinkage overall 12–22%.

VI *Apply the following glaze*

Dry powdered lime	3%	Fire glaze at 1600 °C [1] for 18–20 hr
Dry powdered Zettlitzer kaolin	4%	
Dry powdered quartz	41.8%	
Dry powdered feldspar	32%	
Pre-fired powdered Seilitzer kaolin	19.2%	

[1] At temperatures above 1650°, silica in the glaze reacts with the alumina in the base ceramic and is thereby absorbed so that at these temperatures no glaze can be found on tbe ceramic, after firing.

12.3.IV. *Zircon Ceramics*

In the years shortly before World War II, TELEFUNKEN had already developed a steatite for making brazed ceramic-metal UHF tubes; it was regarded as essential to have a small ZrO_2 content for vacuum-tight bonding of the metal coating (Mo + a few % of Fe) which was sintered on *in vacuo* or in a H_2 atmosphere (PULFRICH). Table T 12–22 gives full details on the manufacture of this ceramic, which in many respects set the

TABLE T 12–21. TYPICAL ANALYSIS OF SOME HIGH-ALUMINA SILICATE CERAMICS (LUKS) [12.3]

TEST No.	COMPOSITION (w/o)									
	Al_2O_3	SiO_2	CaO	MgO	ZrO_2	Fe_2O_3	Na_2O	K_2O	TiO_2	MnO
I	92.08	2.97	1.2	1.55	2.02	0.03	–	–	0.12	–
II	85.64	10.36	1.3	2.45	–	0.02	–	–	0.23	0.04
III	92.95	3.6	2.6	–	–	0.38	0.34	0.04	0.06	–

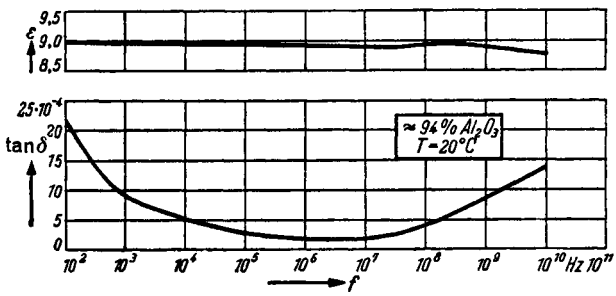


Fig. B 12-41 Dielectric constant ε and loss angle $\tan\delta$ of a high-alumina ceramic (*ca.* 94 % Al_2O_3) at room temperature, plotted as functions of frequency f (LUKS)

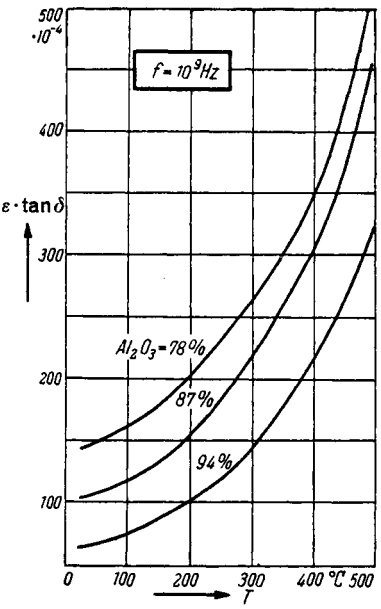


Fig. B 12-42 Dielectric loss coefficient $\varepsilon \cdot \tan\delta$ of alumosilicate ceramics of various Al_2O_3 content, plotted as functions of temperature T at 10^9 c/s (LUKS)

standard for the production of vacuum-tight, brazable metalized ceramics; the most important properties that can be achieved with this ceramic are also given.

Recently, zircon ($ZrO_2 \cdot SiO_2$) has been added, up to 50% or more, to many porcelain and steatite batches (see, e.g., [1,2]RUSSELL, [3]SMOKE). This material reduces expansion coefficients (cf. Table T 12–5 and Fig. B 12-14) and thus considerably increases thermal shock resistance (Table T 12–6). Also, such batches have a much longer sintering range than steatites which makes fabrication cheaper since they can be produced in large lehrs (tunnel kilns) with few rejects. The firing temperature is 1250–1350° according to

TABLE T 12-22. MANUFACTURING SCHEDULE FOR THE VACUUM-TIGHT TELEFUNKEN CERAMIC DESIGNED FOR METALIZING WITH Mo (PULFRICH)

[12.3]

Ⓐ *Batch*

10.2 kg steatite	82.5 %
1.44 kg Zettlitzer kaolin	11.65 %
0.48 kg ZrO_2 (1)	3.9 %
0.24 kg potash feldspar	1.95 %
25 liters distilled water	

→ Mix is milled in 60-liter ball-mill with 35 kg unglazed hard-porcelain balls (25 mm dia.) for 18 hr at 48 r.p.m. Then add 15 ml acetic acid, and blunge →

→ Filter off the liquid by filter press or centrifuge. Dry at 120–150 °C → Yield: *ca.* 12 kg dry premix Ⓐ

Ⓑ *Plasticizing and densification of Premix A*

3 kg premix Ⓐ	
3 kg hard-porcelain balls 25 mm dia., unglazed	

→ Mill in 15-liter ball-mill for 1 hr at 75 r.p.m. → Pour into 10-liter Al vessel. Add 300 g hard paraffin(2), heat for 15 min at 100 °C, stirring continuously and disperse thoroughly →

→ Sieve hot mass twice through 200 mesh/cm² approx. → Compress in hydraulic press cylinder 50–60 mm dia., 60–70 mm height, at 300 kg/cm² → Crush the block to grit sizing(3)

Ⓒ *Molding, firing and grinding*

Mold the body from grit Ⓑ with a lever press. Fill the mold to a height 2–3 times that of molded body; 300–500 kg/cm² pressure → Fire in elec. or gas-fired kiln on fireclay troughs covered with quartz sand(4). Heat-up time 6 hr, firing time 3 hr, at 1350 to 1400 °C, varying with purity of steatite used(5) → After cooling, grind surfaces to be metalized to ± 0.1 mm. Porosity test: immerse in dil. red ink, wash at once in H_2O, dry in oven at 100 °C. Visual test for pores and cracks

Ⓓ *Properties of finish-fired ceramic*

Porosity	%	0
Max. working temp.	°C	> 500 (6)
Bend strength	kg/mm²	18–20
Thermal expansion coeff.	10^{-7}/°C	65–70 (7)
Dielectric constant ε	—	5.5, at 10^7 c/s
Dielectric loss angle	10^{-4}	$\tan\delta$ at 10^7 c/s = 6–8
Vacuum tightness	—	For wall-thicknesses above 3–4 mm, vacuum-tight; otherwise slight gas leakage through cracks

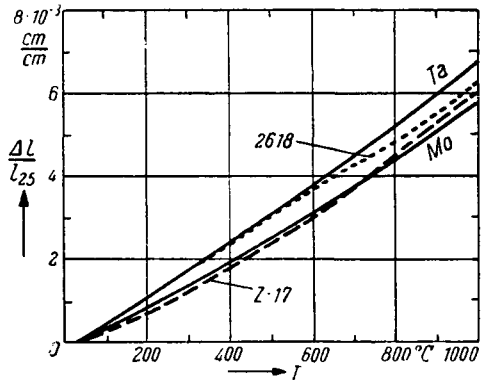


Fig. B 12-43 Thermal expansion characteristics of zirconia ceramics

Zircon talc No. 2618 (dotted curve from [2]NAVIAS) and Zircon Z-17 (dashed curve from NOLTE), compared with curves for Mo and Ta

[12.3]

TABLE T 12–23. COMPOSITION AND SOME PROPERTIES OF A VACUUM-TIGHT ZIRCON-TALC CERAMIC 2618 ([2]NAVIAS)

1	Composition of batch	w/o w/o w/o w/o w/o	Zircon Talc BaF_2 Clay Bentonite	53 32 5 7 3	Analysis see No. 2 below See Table T 12–19, No. 2 – See Table T 12–19, No. 4 See No. 3 below
2	Zircon ($ZrO_2 \cdot SiO_2$)		Type: G.S.; supplier: Titanium Alloy Mfrg. Div. of the NATIONAL LEAD Co.		
3	Type of bentonite		Wyoming		
4	Firing temperature to sintering point	°C	1325 (2 hr in air)		
5	Bend strength	kg/mm^2	14.1		
6	Expansion coeff. 25–300 °C 25–500 °C	10^{-7}/°C	55.4 58.7	} see also Fig. B 12-43	
7	Electrical resistivity	Ω-cm	See Fig. B 12-39		
8	*Te* value	°C	*ca.* 850		
9	Dielectric constant ε	–	7.51 at 10^{10} c/s		
10	Diel. loss angle tan δ	10^{-4}	26 at 10^{10} c/s		

Footnotes to Table T 12-22

(1) ZrO_2 content, according to PULFRICH, is essential for subsequent metalizing with Mo, but this is questionable.

(2) M.P. 52–56 °C.

(3) This process is necessary to avoid air inclusions during later molding.

(4) According to HUNT, in a N_2 atmosphere of 30 Torr.

(5) Shrinkage after firing is 12–18% along the axis of molding (compression), 10–16% perpendicular to this axis.

(6) In electron tube manufacture, i.e. brazing, the ceramic is heated to 800–1000°, during pumping, degassing and aging, up to 500°, and in operation many ceramic piece-parts reach 400° in air.

(7) Suitable brazing partners, internal and external: FeNi (58/42) and (52/48).

the batch, and the sintering range is 30–50°. However, since their dielectric properties are generally worse than those of special steatites in spite of additions of alkaline earth oxides, they are thought of rather as competitors with hard porcelains since they have similar workability but better mechanical and electrical properties by comparison.

TABLE T 12–23A. COMPOSITION AND SOME PROPERTIES OF A VACUUM-TIGHT ZIRCON-TALC CERAMIC (THIESS)[1]

[12.3]

1	Composition of the batch	w/o	Zircon ($ZrO_2 \cdot SiO_2$)	55
		w/o	ZrO_2	10
		w/o	Talc	22
		w/o	Clay	4
		w/o	Barium carbonate	6
		w/o	Borosilicate glass frit (as per Nos. 2 and 3)	3
2	Starting materials for the glass frit, fusing at 1110 °C	w/o	Boric oxide	46
		w/o	Calcium carbonate	32
		w/o	Magnesium carbonate	8
		w/o	Aluminium silicate (clay)	5
		w/o	SiO_2	9
3	Composition of the fused frit	w/o	SiO_2	18.5
		w/o	B_2O_3	42.5
		w/o	Al_2O_3	3.5
		w/o	CaO	29.5
		w/o	MgO	6.0
4	Firing temperature of batch (No. 1) to sintering point	°C	1370–1400	

Properties of the fired ceramic

5	Thermal expansion coeff. (25–500 °C)	10^{-7}/°C	56[2]
6	Dielectric constant ε	–	7.4–7.8 at 10^6 c/s
7	Dielectric loss angle $\tan\delta$	10^{-4}	5.9–7.6 at 10^6 c/s

[1] Roughly the same as zircon ceramic Z-17 and ceramic Z-17 A of the GENERAL ELEC. CO.

[2] Can be sealed via CORNING glasses 7040 or 7050 (see Table T 10–4, A 1) to Mo or Kovar.

Sintered ceramics made of zircon and talc show an extensively crystalline structure with a small glass phase component and can very well be used for vacuum-tight tube parts, especially those that can be metalized with MnMo (20/80) (see, e.g., NOLTE, further details in Chapter 32). Tables T 12–23 and T 12–23A summarize compositions, of the starting batch and raw materials, firing temperatures and chief properties of two typical zircon-talc ceramics. As can be seen by Fig. B 12-43, αs of such ceramics coincide approximately with that of Mo.

TABLE T 12–24. COMPOSITION AND SOME PROPERTIES OF AN ALKALINE EARTH PORCELAIN ([1]RIGTERINK)

1	Composition of batch	w/o w/o w/o	Florida kaolin 50 Flint 15 (325 mesh/inch) Flux (see No. 2 below) 35	
2	Flux (fused at 1200 °C, then milled to 200 mesh/in.)	w/o w/o w/o w/o w/o	Florida kaolin 40 $MgCO_3$ 15 $CaCO_3$ 15 $SrCO_3$ 15 $BaCO_3$ 15	[12.3]
3	Firing temperature (holding time at least 3 hr)	°C	1200–1250	
4	Sintering range	°C	15	
5	Analysis of finish-fired ceramic	mol-% mol-% mol-%	SiO_2 61.7 Al_2O_3 19.2 MgO, CaO, SrO, BaO: 19.1 total (6.7, 5.7, 3.8, 2.9 respectively)	
6	Density	g/cm^3	2.7	
7	Expansion coeff. 25–300 °C 25–600 °C	 10^{-7}/°C 10^{-7}/°C	 33 41	
8	Thermal shock resistance	–	Excellent, goes with small α	
9	Electrical resistivity 125 °C 175 °C 225 °C 275 °C 325 °C	Ω-cm Ω-cm Ω-cm Ω-cm Ω-cm	10^{14} 10^{13} 10^{12} 10^{11} 1.75×10^{10}	
10	Dielectric loss angle tan δ		10^5 c/s	10^6 c/s
	25 °C 250 °C 350 °C	10^{-4} 10^{-4} 10^{-4}	5.4 62.5 250	4.6 35.4 111

12.3.V. *Alkaline Earth Porcelains*

These materials have been developed in the last decade, especially in the USA, for electroceramic purposes. The alkali feldspar of ordinary porcelain is replaced by alkaline earth oxides ([1]RIGTERINK). They have the same low dielectric losses as Mg-silicates, but higher thermal shock resistances. Table T 12–24 contains an example of a material of this type, its composition, firing temperature and chief properties.

12.4. Surface Treatment of Silicate Ceramics

12.4.I. *Cleaning*

Just as with glass, careful surface cleaning is required before use of ceramic components in electrode system construction. The best way to remove organic surface contamination is to heat the ceramic body for 2 hr at 800–1000° in an air-atmosphere furnace; all contact between the ceramic and bare fingers should be avoided. As in cleaning glass, alkaline solutions (10.4.I) will clean ceramic surfaces, and are followed
[12.5] by 2–5 min immersion in dilute HNO_3 and then rinsing in aq. dest. and alcohol. Chromic acid and other cleaning agents for glass may also be used (see 10.4.I).

12.4.II. *Metalization*

This is carried out as a rule by the same methods as for glass, in particular the following:

1. The process for firing noble metals (platinizing, silvering, etc.), to produce conducting or soft-solderable layers; see 10.4.II and III. There is a manufacturer of noble-metal preparations specially suited to metalizing ceramics, the DEUTSCHE GOLD- UND SILBERSCHEIDEANSTALT (DEGUSSA), Abteilung Keramische Farben, Frankfurt/Main. Examples of their products are: (a) "Poliersilber 103"; Ag based, applied by brush, air-brush (spray gun) or dipping; consumption is 1–2 g/100 cm^2; fired normally at 750–850° which can give about 0.01 Ω/square; and (b) "Polierplatin 125"; Pt-based, applied by brush, fired at about 800°, consumption 1 g/cm^2, fairly resistant to soft solders.
2. Cathodic sputtering: see 10.4.IV.
3. Vacuum evaporation (Ag, Au, Al, etc.): see 10.4.V.
4. Spraying by SCHOOP gun, of metals such as Cu. See 10.4.VI. This process gives poor adherence to non-porous ceramic, but this can be improved by pre-spraying with Zn; as Zn has a high VP, this pre-spray is only possible for surfaces that will not be placed in a vacuum.
5. Graphitizing: see 10.4.VIII.
6. Application of conducting lacquers to exterior surfaces: see 10.4.IX*a*.
7. Dry-filming: see 10.4.XIII, 12.2.XI (especially Figs. B 12-20 and B 12-21).
8. Sintering brazable layers of Fe, Mo, MoMn, Ti, Zr, etc. (BONDLEY, BURNSIDE, PULFRICH, [2]VATTER, etc.), to produce vacuum-tight, high temperature resistant, ceramic-metal joints: see Chapter 32 "Ceramic-metal Joints".

In many cases it is recommended that, before metalizing, the ceramic surface is grit-blasted with SiC or Al_2O_3 (corundum) and/or given a 1 min dip in 50% HNO_3 plus a thorough washing in distilled water.

12.5. Application of Silicate Ceramics in Vacuum Technology

If one first considers the question of the advantages and disadvantages of using these ceramics in HV technology both for insulator components and for vacuum-tight envelopes, compared with other insulators (especially glass and mica), the tabulation appears as follows:

(α) *Advantages of ceramics*

1. Refractoriness; they usually stand temperatures above 1000°; thus, up to such temperatures they do not deform (e.g. in soldering or degassing processes) and do not experience devitrification like glass, or calcination, like mica; therefore
2. High degassing temperatures (650° and more) compared with glass (350–360°) or mica (600°), hence more intense and shorter period degassing is possible (specially striking in the case of porous internal piece-parts).
3. In contrast to glass, much greater wall-thicknesses are possible without danger of cooling stresses, as a result of which ceramic components have greater mechanical strength, which can be achieved in particular with all-ceramic tubes of the type seen in Figs. B 12-53 or B 7.2-20; this is specially important in cases of intense vibration and shock loading of military electron and gas-discharge tubes. [12.5]
4. Ceramics, even those with appreciable glass-flux content, have high electrical resistivity even at elevated temperatures, because of low alkali content; lower dielectric losses can be achieved than with glasses, even at H.F.; this allows high temperatures of continuous operation and thus the construction of very small electron devices of high-power rating, while under the same conditions but using glass, effects like electrolysis, polarization at the electrodes and melting could occur, due to large H.F. losses.
5. With the help of fine machining (grinding), very precise electrode spacings (down to ± 0.01 mm) can be achieved—in contrast to glass in particular.
6. The high degree of surface roughness of ceramics gives high surface resistivity, especially in the case of porous material, and this is retained even after prolonged operation with unavoidable electrode sputtering.
7. Thermal shock resistance of porous ceramics is extremely high.
8. Sintering brazable metal layers to the ceramic permits manufacture of vacuum-tight lead-ins which will carry heavy currents and operate at high temperatures. By proper selection of the ceramic material, a good expansion match between metal and ceramic can be achieved.
9. Ceramics have great chemical stability. They are inert to atmospheric weathering, tropically resistant, and resistant to chemical attack, with but few exceptions.
10. The price of ceramic components of equal thermal and electrical capacity is less than for fused quartz.

(β) *Disadvantages of ceramics*

1. Higher cost of manufacture of starting materials due to greater outlay on homogenization, i.e. comminution, mixing, deaeration, as compared with glass ("purification" in the glass-melting furnace); there are greater tool costs and longer manufacturing times than for glass-working, and the loading factor of the ceramic-firing kiln is lower than for glass furnaces.
2. Relatively complex and expensive forming processes for semi-finished products, since thermoplastic working as is used for glass or quartz is not possible both because of the low glass content of ceramics and for structural reasons; nor is punching possible as it is for mica.

3. Raw-working of ceramics with its inescapable shrinkage gives dimensional precision of piece-parts that is less than can be achieved by blowing or molding glass, unless finish-grinding is employed.
4. Silicate ceramics like glass are brittle and are sensitive to local mechanical stress, especially notch effect (low tensiles).
5. High surface hardness of internal parts (which may scratch glass) and their lack of elasticity prevents the possibility, so highly valued in the case of mica, of providing a spring bracing for ceramic electrode components, against the glass wall.

[12.5] 6. Low IR transparency of ceramic electron tube walls prevents the possibility of radiation cooling of electrodes (unlike the case of glass walls) and necessitates conduction cooling of hot electrodes by means of metal members.

7. Ceramic envelope or wall sections such as tubes, caps, or disks are only vacuum-tight under certain conditions, in contrast to those made of glass.
8. Production of vacuum-tight lead-throughs in ceramic envelope walls by metalizing and brazing is much more expensive than making vacuum-tight glass-metal seals, and is not suited to automatic mass-production as used for glass.

From this comparison and from the specific properties of silicate ceramics it is concluded that for individual applications the following factors must be considered: degassability, vacuum-tightness, peak operating temperature, mechanical strength, expansion coefficient, thermal conductivity, thermal shock resistance, H.F. losses (at high temperature also) and—particularly with large components—ease of manufacture with tolerable cost. Even the specific manufacturer can be of great importance when considering use of a ceramic for special purposes, because ceramics of the same type but different maker can often possess quite different characteristics and properties; this is due to different sources for the raw materials (minerals from different deposits) and hence unintentional differences in additives and impurities, as well as differences in preparation and firing processes determined by the firm itself.

In the following sections some examples of the application of silicate ceramics are cited, taken from vacuum technology and tube manufacturing practice:

(a) *Insulating components for Hg tank-rectifiers:* because of the size and thickness of these parts and the exclusively low-frequency service ratings on them, they are mostly porcelain with glazed exteriors. Internal surfaces and components for use at elevated temperatures should preferably have their glaze omitted or removed by grit-blasting to improve degassing and avoid dangers of decomposition of the glaze; the same applies for enhancement of the adherence of cemented areas and surfaces due for metalization by SCHOOP gun. A good glaze is, however, needed for the platinum-bright metalizing process.

1. Insulation sleeves for anode leads; in the case of continuously pumped rectifiers, the end flats are ground and sealed by rubber gaskets under compression (Figs. B 12-44, B 8.5-14) or else the glazed ends are platinized and, possibly with the insertion of a flexible metal ring, soft-soldered to the metal tank (Fig. B 9.3-30); for sealed-off Hg rectifiers, the sleeves are brazed, after metalization with Fe or Mo (see Chapter 32). In low-voltage Hg rectifiers, use has been made recently of pressed glass seals with Fe rings (Figs. B 5.3-4B and B 5.3-6B), or Kovar-glass seals (Fig. B 5.3-6A), and other fusion

seal constructions. See, e.g., DOBKE. In direct solid soldering (inelastic joints), care should be taken to see that the ceramic tube, when soldered in, is only subjected to compressive stress (see also 12.2.IV). Contact zones between porcelain and graphite anodes must be kept out of any fields by suitable constructions (formation of recesses as per Fig. B 8.5-15, Vol. 1), since the reduction by the hot graphite of the alkali content of the porcelain can readily produce regions of low electron work function, i.e. arc-back centers, on the rectifier anode.

2. Insulating wells for liquid Hg cathode pools: up to 750 mm dia. or more with Hg pools up to 60 kg, wells glazed on the outside, pre-platinized at the connexion zone and soft-soldered with Sn into the rectifier envelope (see Fig. B 11-21). Direct contact between porcelain and hot arc or cathode spot should be avoided, e.g. by a quartzware insert ring. [12.5]

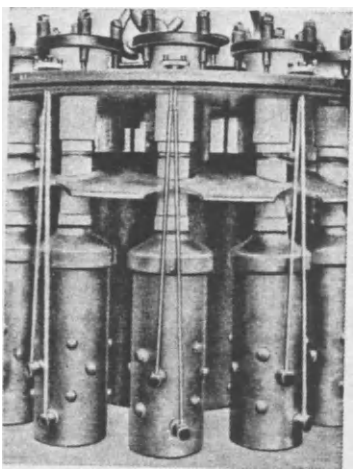


Fig. B 12-44 Cover-plate of a grid-controlled Hg rectifier, with anodes and grids. Anode leads insulated by porcelain sleeves, anode heads made of graphite with guard tubes of Fe, which also support the control grid; in foreground, screened grid leads (made by SIEMENS–RÖHRENWERK) (cf. also BOSCH and Figs. B 8.5-14, B 8.5-15)

(b) *Components for Hg rectifiers with glass envelopes:* screening tubes for the anode leads to prevent arcing (Fig. B 12-45); these sleeve tubes often serve as insulating supports for arc-back or control grid (see, e.g., Fig. B 5.3-7).

(c) *Components in gas-filled discharge tubes* (usually inert gas used)

1. Screening tubes for electrode leads to prevent initiation of gas discharge; example: Fig. B 8.5-19 (left illustration); here the contact area of graphite and ceramic is shielded from the electric field by withdrawal into a narrow recess (No. 3), and scratching by the ceramic of the surface of the glass wrap-sheath on the sealed-in lead-through is avoided by several annular, elastic interlayers of mica (No. 5) which at the same time close off the field.

2. Insulators in glow-discharge tubes, e.g. voltage dividers and rectifiers (see Chapter 26).

3. Components in lightning arresters, e.g. vacuum-tight tubular envelopes made of steatite as in Fig. B 12-46, metalized at the ends by sintered Fe powder and brazed to Ni end-caps (see [2]VATTER, and Chapter 32); or insulators as in Fig. B 12-47 (No. 4) in iron-tube types with pressed glass seals, for centering the internal discharge electrode

(also acting as the pump stem) with respect to the outer electrode (which is also the vacuum envelope).

(d) *Components in Hg switches:* the whole envelope (Fig. B 12-48) can be made from vacuum-tight steatite externally glazed, to which the glass pump stem and electrode

[12.5]

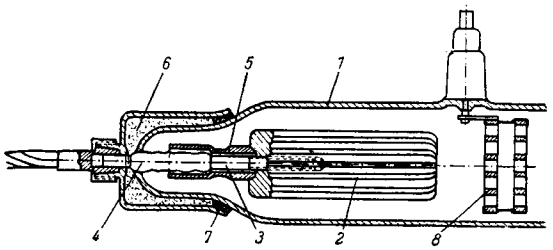


Fig. B 12-45 Cross-section of an anode lead-through for a Hg rectifier (hard glass) with support rod screened by ceramic sleeve (cf. also Fig. B 5.3-7)

1 glass tube; *2* graphite anode; *3* Mo support and current-lead rod, sealed into glass; *4* glass wrap on Mo rod; *5* ceramic guard-tube made of a steatite (e.g. Calit); *6* cap lined with asbestos fiber, for mechanical protection of seal zone and as thermal insulation to prevent condensation of Hg and possible arc-back; *7* cemented zone; *8* grid with separate seal-in connexion

leads can be sealed by means of an expansion-matching glass. In another construction (Fig. B 12-49), a tubular spark-protection tube of steatite or cordierite is sealed only to the part of the inner glass wall where the switching arc occurs. See Fig. B 8.4-10 for the construction of an electro-magnetic Hg switch with sinker, where the inner Hg electrode (No. 3) is insulated by a ceramic dish (No. 4).

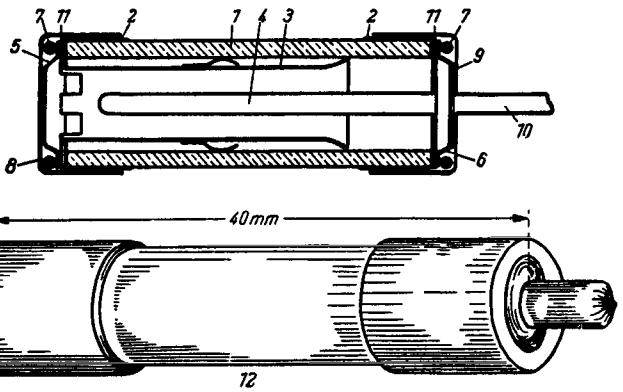


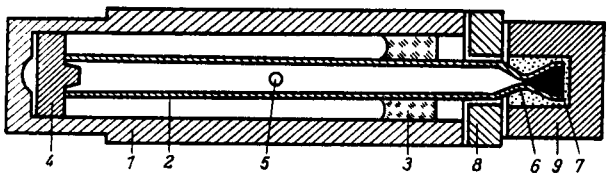
Fig. B 12-46 Inert-gas-filled lightning arrester, with steatite tube (1VATTER)

1 tube of unglazed dense steatite (Calit), 2 mm wall; *2* external metalizings (Fe) on periphery of both ends of (*1*); *3* external tube electrode; *4* inner (rod) electrode; *5* and *6* interposed caps to prevent flow of braze into the envelope; *7* braze ring (AgCu); *8* and *9* cap closures of Ni or Ni-plated Fe; *10* pumping stem silver-brazed to cap *9*, braze joint between ceramic metalization (*2*) and closures (*8* and *9*); *12* exterior view of completed tube sealed off from pump

(e) *Components in HV amplifier and transmitter tubes* (see also BAIER)

1. Supports for electrode system construction: while in Europe punched mica disks have been mostly employed to date, except during World War II when reliable mica

was not always available (see, e.g., LANGER), increasing use has been made in the USA of porous and readily degassed, low-loss ceramic decks, especially in large, high-power HV tubes. This came about after development of precision-grinding techniques had led to success in achieving the close tolerances needed, on a mass-production scale and with acceptable costs (see, e.g., STANISLAW). Thickness tolerance is ± 0.025 mm on



[12.5]

Fig. B 12-47 Lightning arrester ([2]ESPE)

1 Fe tube (1st electrode, also envelope); *2* FeNi (50/50) tube (2nd electrode, also pump stem); *3* pressed glass seal; *4* centering piece, made of porous steatite; *5* pumping hole; *6* crimp-off zone of pump stem; *7* seal-off solder for ensuring vacuum-tightness of crimp; *8* insulating piece, ceramic; *9* protection + electrical-contact cap, soft-soldered to pump stem

minimum deck thicknesses of 0.5 mm, parallelism must be better than 0.0025 mm, the tolerance on hole-diameter is — 0.05 mm, deviation of hole separations from the center axis ± 0.05 mm; for insulator bridges and decks of special steatite DIN Type 240, tolerances on hole diameter and hole separation even of $+0.02$ mm are commercially guaranteed, as of recent date (PORZELLANWERK NEUHAUS). Figure B 12-50 shows the multiplicity of shapes used, and Figs. B 12-51 and B 8.5-22 give examples of ceramic

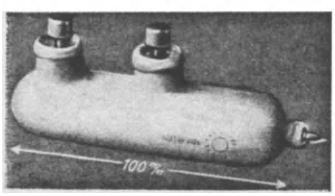


Fig. B 12-48 Hg switch made from vacuum-tight glazed steatite tube (Calit), with glass seals for pump stem and Mo seal-ins (made by MUTH UND CO., Nürnberg)

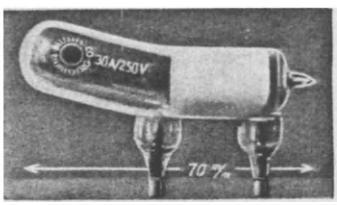


Fig. B 12-49 Hg vacuum switch made of glass (no Hg filling shown) with steatite (Calit) spark protection tube sealed to the inside of the glass; current leads are Mo (made by MUTH UND CO., Nürnberg)

bridges in tubes with graphite anodes. Figure B 3.5-8 A shows supports for electrode systems, made of low-loss steatite, for short-wave oscillator (generator) tubes.

As the cost of the dies is rather high, natural ceramics which can be easily worked are used for distance pieces to test out the shape needed and its dimensions, i.e. for making patterns and first test-models; materials for this are soapstone or pyrophyllite, worked and then fired at 800–1000° to give a small and calculable shrinkage, or machinable, fired ceramics like Ergan or Porolit, which are worked and then heated (without shrinkage) for $^1/_2$ hr in air at 900° to remove organic impurities on the surface. (The latter two materials are porous and therefore cannot be degreased or washed in grease-solvents like trichlorethylene.) For mass-production of ceramic support decks whose

dimensions have been established by test, porous low-loss steatites (e.g. Alsimag 211-S, or those of DIN Type 240) are used. For parts destined to run hot, porous high aluminas (such as Alsimag 393 or 548) are employed; they can be easily degassed at 600–900°.

[12.5]

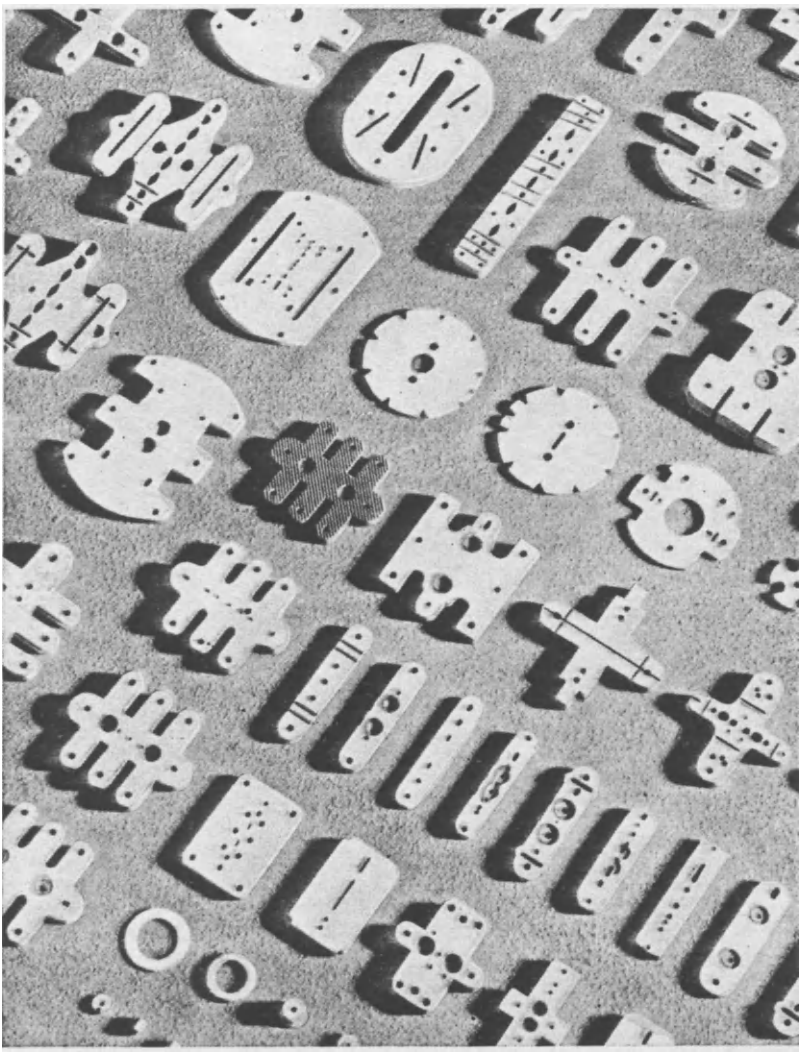


Fig. B 12-50 Insulator and distance pieces and rings of porous ceramic for HV amplifier and transmitter tubes (courtesy of AMERICAN LAVA CORP., Chattanooga, Tenn., USA)

Because of their rough surfaces, these porous ceramics offer less likelihood of forming continuous metallic layers which impair the surface resistivity.

Stray electrons that strike ceramic bridge insulators of HV amplifier tubes near the control space, can give rise, as they would with mica or glass bridges, to noticeable

disturbances (ambiguous or poorly reproducible tube characteristics, reduction of internal resistance, interelectrode capacitance changes, etc.) as discussed by MOLTHAN. If the compact nature of the construction does not permit arranging the insulators far enough from the control space of the tube, it is recommended that they be screened off by metal mesh or sheet, tied to cathode potential (JOBST).

Combinations of ceramic and mica bridges have also been used in practice; electrodes specially sensitive to gap variations (cathodes and control grids) are held by mica sheet pieces fastened to the ceramic bridge by hollow rivets, while the generally less precisely-made ceramic serves to hold the heavy, hotter anode. Springy mica tongues which touch the glass wall can be fixed to the ceramic electrode-support in the same kind of way (see, e.g., Fig. B 13-26). [12.5]

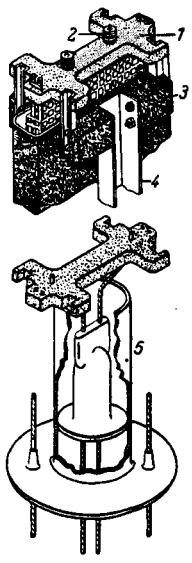


Fig. B 12-51 Ceramic piece-parts in a small transmitter tube

1 deck of porous ceramic; *2* cathode spring tensioning; *3* graphite anode; *4* support channel section made of Mo; *5* glass foot

2. Insulating caps (petticoat insulators) in amplifier tubes to avoid failures of insulation caused by evaporated cathode or getter material (Fig. B 12-52). These caps can be pinched directly into the foot-glass when making the pinch.

See 10.4.XII and Chapter 13 on improving insulation of glass pinches and mica support disks by application of powdered oxides.

3. Envelopes for UHF transmitter tubes, simultaneously providing insulation between electrodes, which are brazed with annular flanges to the premetalized ceramic. Originally, low-loss steatites with a small amount of ZrO_2 were used (Table T 12–22) (PULFRICH-TELEFUNKEN). Later on, forsterites were developed for this (Table T 12–19, $\alpha \approx 90\text{–}110 \times 10^{-7}/°C$), as were alumosilicates (Table T 12–20, $\alpha \approx 60\text{–}90 \times 10^{-7}$) and high-zircon steatites (Tables T 12–23, $\alpha \approx 45\text{–}60 \times 10^{-7}$).

4. Parts for stacked tubes: efforts towards automation in electron tube construction, especially in USA, have recently led to the development of the "stacked tubes". Figure B 12-53 shows a scaled-up model in which, apart from the metal electrodes, only ceramic

parts are used both for insulation and support of the individual electrodes. As shown in Fig. B 12-54, in these all-ceramic tubes the electrodes are interleaved with ceramic distance pieces and are threaded on two straight support rods sealed into the ceramic foot in glass beads, for example. The current leads to the electrodes stem from other electrodes sealed through the foot; after assembly, and pumping (in a bell-jar) are complete, the envelope, also made of ceramic, is brazed vacuum-tight to the ceramic foot either by solder glass or braze. If a braze is used, the brazing surfaces are premetalized. These tubes can be assembled, pumped and formed wholly on automatic machines,
[12.5] and have the advantage of greater precision in electrode gapping. They can be heated almost to 900°, and degassed at that temperature. The thickness of the ceramic distance

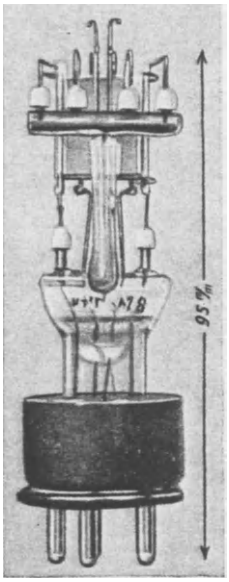


Fig. B 12-52 Oxide cathode amplifier tube with porous porcelain caps to increase surface insulation between lead-wires

pieces and hence the separation between electrodes can be held to a precision of 0.0125 mm, while the precision attainable in gapping support holes in mica disks is only 0.025 mm, apart from the fact that even this cannot always be held in assembly because the holes may open out, nor in operation because of possible decomposition of the mica. All-ceramic tubes were conceived mainly for military purposes; they will stand temperatures from —195° (liquid air) to 100° (boiling water) and repeated thermal cycling from 20° to 450° in an air oven. Figure B 12-54A shows a similar tube by EIMAC, made of high-alumina silicate ceramic.

5. Ceramic UHF power-output windows. These are metalized at the edge and brazed vacuum-tight and then serve to transmit H.F. power from magnetrons or klystrons to hollow waveguides connected to the electron tubes (see, e.g., HYNES); the preferred material for such purposes is high-alumina ceramic with low ε and $\tan\delta$ that will stand elevated temperatures, either in the form of very accurately plane-parallel-ground

round or rectangular plates. A typical case would be one 25 × 50 mm, 0.75 mm thick, metalized and then brazed at the edge to Kovar (Nilo K) with Cu, CuAu or NiAu. Synthetic sapphire disks are also successfully used, 25 mm dia., sealed to NiFe by solder glass or, after Mo-metalizing the edge, brazed thereto. Recently, conical windows have been employed (Fig. B 12-55). The ceramic must be very pure. Above all, there should be no Fe particles in it, or hot-spots rapidly form, due to the H.F. field, which give rise to cracks in the ceramic caused by thermal shock and the tube may leak.

[12.5]

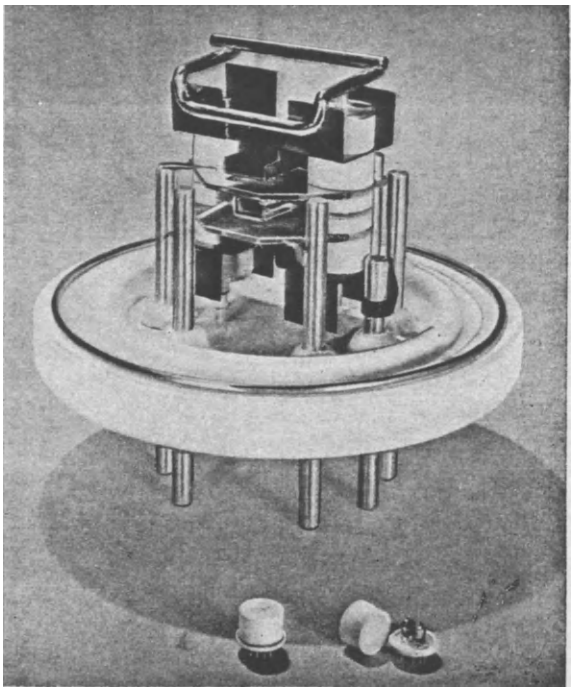


Fig. B 12-53 Model (10 to 1 scale-up) of a double triode, made by superimposition of 10 sections (so-called "stacked tube"). Foot and insulating distance pieces are ceramic. Type SN 1724 D

When cathode heater has been installed and shorted turn for getter-flashing has been attached, the tube is ready for pumping under a bell-jar; the ceramic envelope is then sealed to the foot. In the foreground the tube is shown actual size (*ca.* 16 mm dia.), both opened and sealed-off (courtesy of SYLVANIA ELECTRIC PRODUCTS INC., Bayside, N.Y., USA)[1]

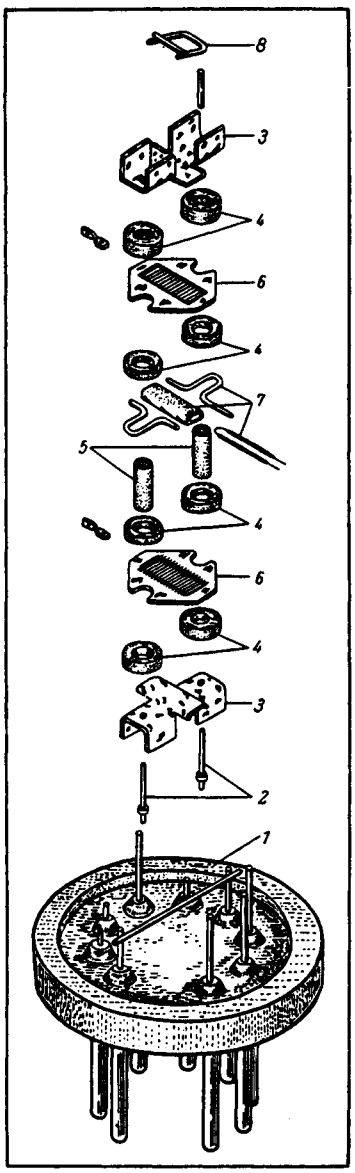
[1] For pumping and seal-off procedure for similar ceramic tubes without pump stems, see also TELEFUNKEN.

(f) *Components for CRTs, TV and radar tubes*, mainly in the form of rods to act as insulating supports for metal piece-parts and possibly the deflexion system (gun). Figure B 12-55A shows an example of such a construction, and other examples are given in Figs. B 8.5-28 and B 5.2-16. See Fig. B 5.5-8 for the ceramic parts of the cathode of a gas-filled CRO (high-voltage ion tube).

(g) *X-ray tube parts.* Examples: shafts (Calit) for rotating anodes (Fig. B 12-56); vacuum-tight insulator pieces for cathode and anode of demountable, continuously

pumped experimental tubes (Fig. B 6.3-8). Use of gas-tight ceramics also permitted the very compact construction of modern surface (contact) therapy tubes with vacuum-tight brazed-in Be windows (Fig. B 5.6-10, Nos. 4 and 8).

[12.5]



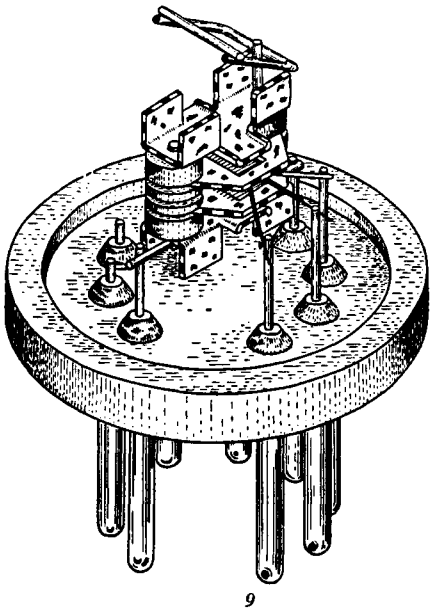


Fig. B 12-54 Components and assembly of a stacked tube (see Fig. B 12-53 for model) (PALMER)

1 ceramic foot with sealed-in lead-throughs; *2* support rods; 3 anode plates with cooling flags; *4* ceramic distance pieces; *5* ceramic insulator sleeves; *6* grid plates; *7* I.H. oxide cathode with heater and support stirrups; *8* H.F. shorted turn with getter bridge; *9* stacked assembly after welding on the connexion wires.
Translator's note: components are threaded over supports (2)

(h) *Vacuum-tight envelopes for betatrons.* ("Electron accelerators"): either glazed porcelain is used (Table T 12-13, No. 5 + glaze) which can be sealed to Mo-sealing

glasses (e.g. CORNING 7050) to make a tight, strong joint, or glazed steatite as in Fig. B 12-57 (see Chapter 32 for details of ceramic-glass seals). To avoid harmful inner wall-charge accumulation, HURSH recommends a commercial Pt or Pd luster diluted with acetone and fired on (see also 10.4.II).

(i) *Vacuum-tight envelopes for Geiger counters* with mica windows (see, e.g., ANTON; ceramic-metal seals are made with dry-milled glass powder, sieved through 100 mesh/in. screening).

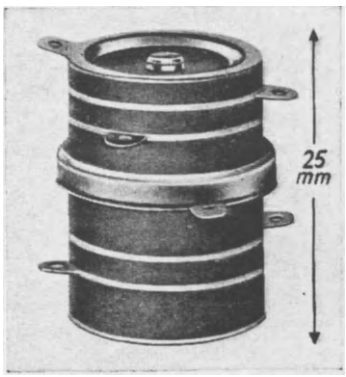
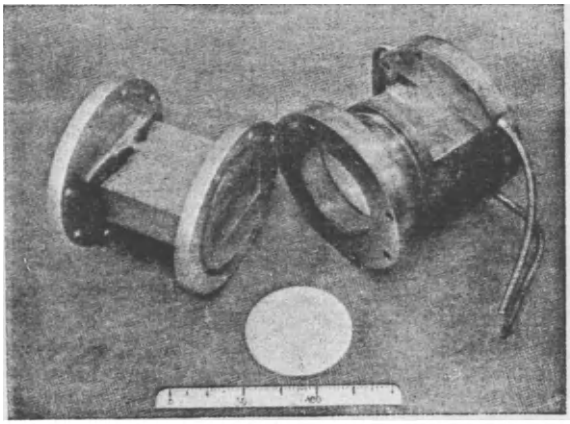


Fig. B 12-54A Shock-proof tube made from high-alumina silicate ceramic. (All-ceramic double triode type 33 C 3 A 2, made by EIMAC; cf. [2]ANON. Life exceeds 25,000 hr, max. operating temperature 500° for life quoted)

[12.5]



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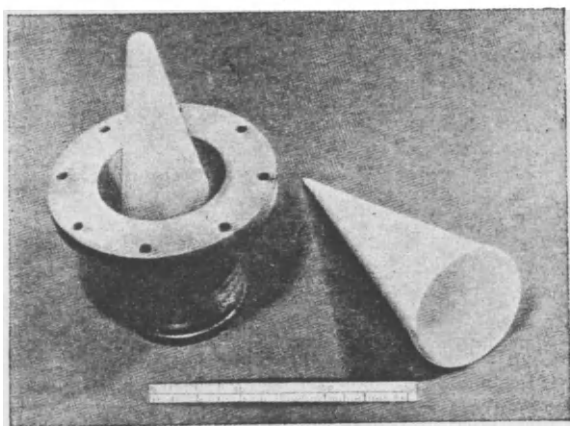


II

Fig. B 12-55 UHF power-output window made of high-alumina ceramic (LA FORGE)
I plane-parallel ground disk (72 mm dia.)
II conical window for a klystron operating at 10 cm wavelength (base of the cone about 80 mm dia.)

(k) *Support rods for special filament lamp mounts*, particularly for projection purposes (see Fig. B 12-58).

(l) *Gas inlet valves with porous ceramic bodies*, sealed into glass and covered by Hg to make a vacuum-tight closure and control the flow. Figures B 12-59 and B 12-60 show two types. The first appears to have the advantage, since no long Hg column is needed for closure and it can be used when the gas reservoir is filled to atmospheric pressure. With this valve it is possible to hold vacua from 5×10^{-7} to 5×10^{-3} Torr at pumping speeds of 2–3 liters/sec (MORRISON).

[12.5]

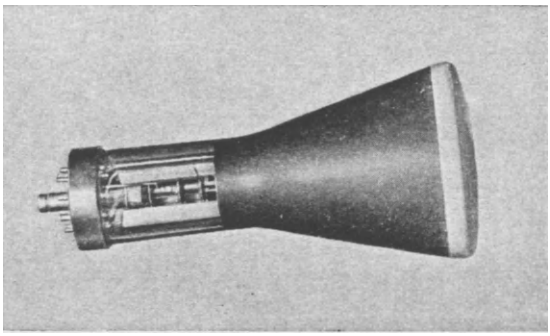


Fig. B 12-55 A Small oscillograph tube with ceramic rods (as per Fig. B 10-277) to support the whole electrode system (electron beam source and deflector plates) (courtesy of PHILIPS, Eindhoven)

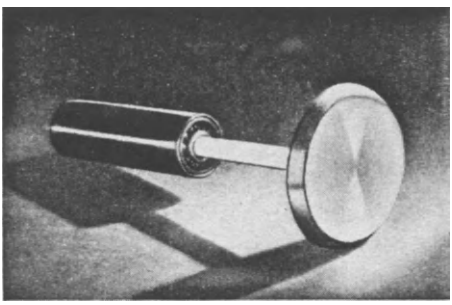


Fig. B 12-56 Rotating anode of an X-ray tube with a Calit ceramic shaft (courtesy HESCHO, Hermsdorf, 1953). Cf. also Figs. B 3.2-28 and B 5.2-17

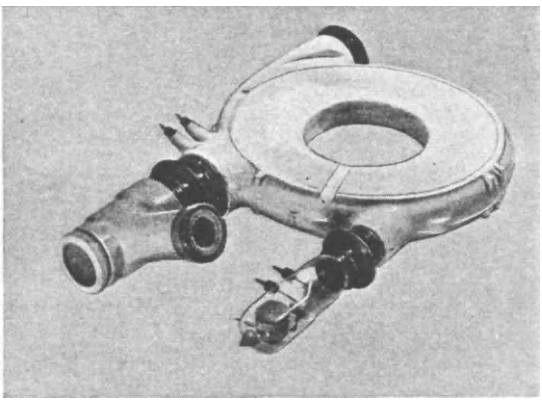


Fig. B 12-57 Ceramic vacuum envelope for a 15 MeV betatron (electron accelerator) with sealed-in glass system (courtesy of SIEMENS REINIGER WERKE, Erlangen). Ceramic is glazed special steatite made by STEATIT MAGNESIA A.G., Lauf in Bayern (see also GUND, SCHITTENHELM, SOYCK)

(m) *Support and distance pieces* of steatite in sealed-off resistance thermometers of the type shown in Fig. B 4.1-9 (No. 3).

(n) *Tube sockets (bases) and holders* of low-loss, soft-glazed steatite for H.F. and UHF tubes (Fig. B 12-60A).

(o) *Piece-parts for vacuum furnaces*

1. Vacuum-tight furnace tubes up to 200 mm dia., 1.5 m long. Examples: vacuum furnaces for first degassing processes, with vacuum-tight ceramic tubes (see, e.g., Fig. B 9.2-8), heated by heater wire or strip wound directly on the outside of the tube. Up [12.5]

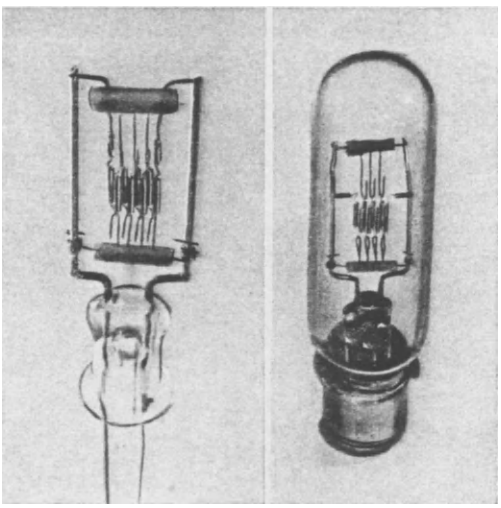


Fig. B 12-58 Tungsten coiled filaments for film projector lamp, supported by hooks mounted on ceramic bridges (courtesy of PHILIPS, Eindhoven)

I from MANDERS; II from KOTTE; cf. also Figs. B 8.5-29 and B 10-229

I II

to 1100° hard porcelain is good enough, or better still, zircon tube; for higher temperatures, high-alumina ceramic tubes have to be used, with Ta windings and no protective gas up to 1300°, with Mo winding in protective atmosphere up to 1500°. At still higher temperatures, one must go over to pure oxide ceramics (q.v. in 12.6).

2. Hydrogen stoves for degassing up to 1000°, with ceramic tubes as per Fig. B 9.2-16, II. Blackening ovens up to 1000° max., ceramic tubes, see Fig. B 9.4-14. Insulators for heater coils; used in nichrome-wound tube furnaces as in Fig. B 9.2-7A (No. 3).

3. Insulating pedestals in H.F. reduction furnaces with bell-jar, to support induction-heated crucibles (see Fig. B 7.3-1, No. 13), or suspension base (and radiation shield) in H.F. degassing units to carry the work-holder (see Fig. B 9.2-13, I, especially No. 2); for temperatures above 1500°, it is better to use pure oxide ceramics for this.

4. Crucibles for non-ferrous metals in vacuum induction furnaces (e.g. Figs. B 6.1-17, No. 2; B 9.2-3, III) at temperatures sufficiently low that there is no fear of take-up of crucible material by the melt; otherwise only suitable pure oxide ceramics can be considered for crucibles (see 12.6).

[12.5]

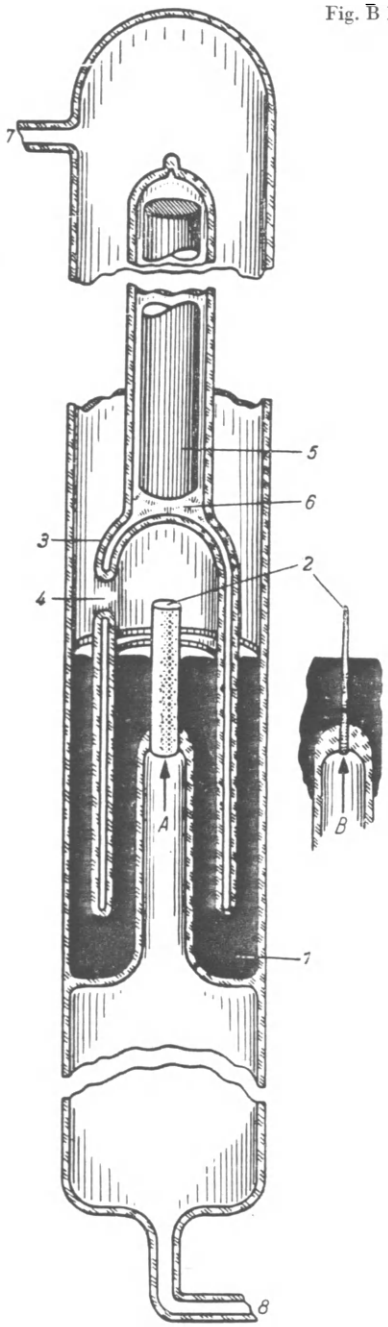


Fig. B 12-59 Gas inlet valve with diffusion rod made of porous ceramic and sealed into the glass; gas flow rate can be controlled by a Hg level which is set electromagnetically (MORRISON)

1 Hg; *2* porous ceramic rod (*A*: 6 mm dia.; *B*: 1.5 mm dia.); *3* glass sinker with orifice *4*; *5* Fe core in glass wool *6*; *7* line to gas reservoir; *8* connexion to pump and vessel

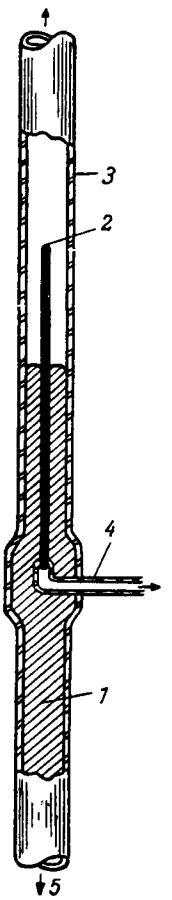


Fig. B 12-60 Gas inlet valve made of glass, with porous ceramic rod and Hg cut-off (HAGSTRUM)

1 Hg; *2* rod (*ca.* 1.5 mm dia., 125 mm long) of porous ceramic, e.g. Stupakoff no. 1646, sealed to Pyrex CORNING 7740 via an intermediate glass; *3* glass tubing connexion to gas reservoir; *4* ditto to vacuum system; *5* ditto to Hg reservoir for setting Hg level

(p) *Holders for glass sealing devices:* see, e.g., Fig. B 5.4-13, No. 6.

(q) *Brazing jigs* (finish-ground to exact dimensions), since ceramics are not wetted by solder even when the operation is carried out in a reducing atmosphere, so that the work does not adhere to a ceramic jig as it might to metal ones.

(r) *Ball-mills:* for milling glass powder, suspensions of phosphors (see, e.g., Fig. B 15-2, No.4), oxide cathode paste, and other auxiliary materials or chemicals needed in tube manufacture. When milling (hard) ceramics, care should be taken that undesirable impurities (SiO_2, alkalis) are not introduced into the mill-batch by abrasion of the mill walls and the balls. [12.6]

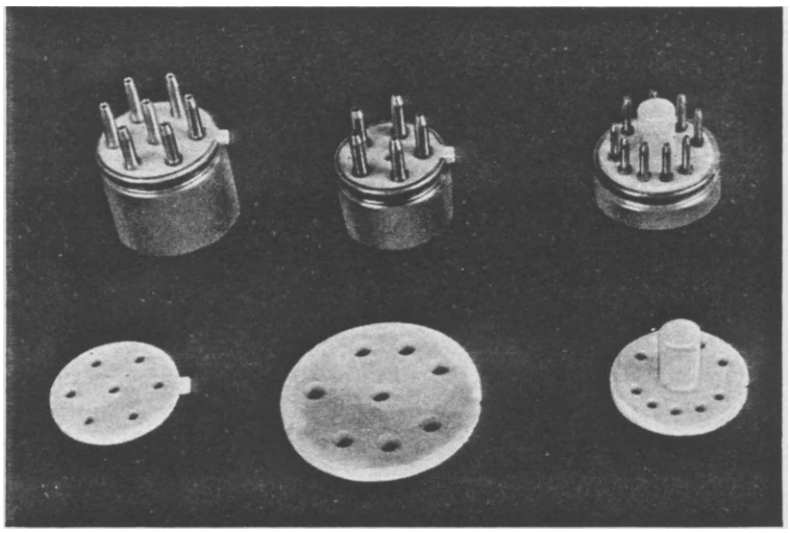


Fig. B 12–60A Tube sockets (bases) and holders of low-loss, soft-glazed steatite for H.F. and U.H.F. tubes (courtesy of PORZELLANFABRIK NEUHAUS).

12.6. Pure Oxide Ceramics

([2]JAEGER, JOHNSON, NORTON, PALATZKY, PECHMAN, RUSSELL, [1,2]RYSCHKEWITSCH, WARDE, [1,2]WHITTEMORE)

Pure oxide ceramics must be used in all cases where the softening point of high-alumina silicate ceramics (which is fairly high), or their chemical resistance, is not sufficient; examples are high-temperature furnace tubes, crucibles for melting, and electron-tube components for high-temperature service. Theoretically, such ceramics have no silicate frit added, but in practice a less sharp distinction is drawn between low-silicate and silicate-free materials: many commercial products offered as "pure oxides" in fact contain small amounts of silicate frit (natural soapstone, talcum, Al-silicate) to reduce their sintering temperature, i.e. to cheapen their manufacture. DIN 40685 therefore refers to the groups of materials 710, 720 and 730 "as products of highly refractory, *almost* pure oxides" (see Table T 12–10D).

These ceramics consist of a more or less dense structure of high-melting oxide crystallites (Al_2O_3, MgO, ZrO_2, BeO, ThO_2 or mixed oxides like $Al_2O_3 \cdot MgO$) which coalesce by recrystalization during the firing process, but below the M.P.s of the oxides concerned (RUFF). They are mostly unitary systems and possess the highest M.P.s of all insulators, and even at elevated temperatures generally have a very large insulation resistance (see Fig. B 12-67).

Manufacture of oxide ceramics at many points differs essentially from that of silicate ceramics:

[12.6] (a) Primarily, and in contrast to the latter materials, the oxides are obtained synthetically by chemical processes and usually have to be analysed for small amounts of impurity (mainly lime, alkalis, soluble salts and Fe_2O_3). Before processing, the starting oxides are often first heated for several hours in air at 1000° to remove H_2O and CO_2, then in a hydrogen stove in suitable ceramic crucibles to 1600° to evaporate alkali-Mg-silicates and alkali salts. The material sinters in this process and develops a white crystalline appearance. Use may also be made of arc-melted and purified material. Oxides so treated are then crushed and ball-milled to fine particle size, all contact with metals being avoided.

(b) The powdered oxides are plasticized with a fluid (usually water) and this presents many more difficulties than occur with silicate ceramics, which have a plasticizer content of ball-clay, talc, bentonite and such like. The starting material must above all be comminuted down to at least 5 μ grainsize. This is the *first* prerequisite for plasticizing the batch since adsorption bonds between make-up water and powder grains depend strongly on the grain-size. These adsorption forces act so as to surround each particle with a liquid skin which makes possible a mutual slip of the particles, but without loss of coherence. Since, clearly, the coherence of the mass is better the more strongly the fluid medium is bonded to the particles, the *second* prerequisite for good plasticizing is the use of suitable make-up fluid with strong bonding (wetting) to the grains of properly comminuted ceramic; a guide here is the experimental fact that wetting is best if both fluid and grain have similar molecular structure, and in the case of the well-known ceramic oxides examples of wetting fluids are H_2O, alcohol, glycerine, and other multivalent alcohols. Further, polar materials such as stearic acid will assist wetting by water, the COOH group bonding to water molecules, the residual hydrocarbon bonding to materials that in the ordinary way are wetted with difficulty or not at all by water.

Care has to be taken that the mill-batch is not contaminated by material from the mill wall such as SiO_2 or alkalis, which can much impair the thermal and particularly the electrical properties of the end-product. Therefore "electrically sensitive" ceramics are best ground in steel mills with steel balls, and Fe ground into the batch can be removed reliably by washing in HCl after milling, since the oxides (with the exception of MgO and to a lesser extent BeO) are virtually insoluble in hot dilute HCl and at most are superficially etched (see below). The previously mentioned vibration ball-mills have proved particularly good for fine-grinding; a trough-shaped container is filled with mill-batch and steel balls of 1–2 mm size, supported on a spring mount, and vibrated 5–6 times/sec by an eccentric cam attached to the shaft of an electric motor. This produces continuous abrasion of the mill-batch internally, on the walls, and by the balls,

and the number of ball collisions per unit time is 20–30 times higher than that in the ordinary rattler (drum mill) and so the vibration mill is correspondingly more efficient than the conventional crusher.

Plasticization of the batch can also be improved by etching the grain surfaces with HCl or other acids, just as with low-clay silicate ceramics. This results from the increase in surface area of the oxide crystallites, and also from the effect of the resulting oxychlorides (e.g. $AlCl_2OH$), which adhere very well to the surface of the solid oxide grains

[12.6]

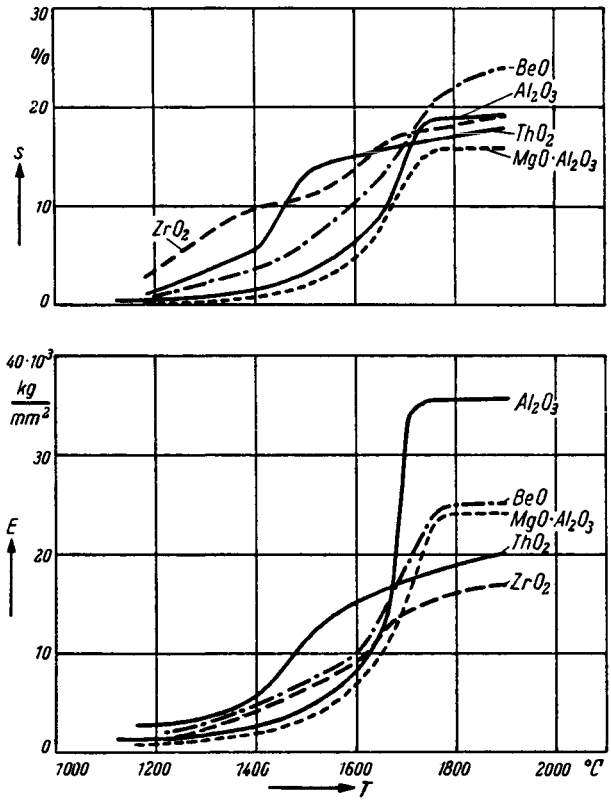


Fig. B 12-60B Young's modulus E and firing shrinkage s of various high-fired pure-oxide ceramics, as functions of firing temperature T ([1]RYSCHKEWITSCH)

and are bonded to the make-up water molecules by the OH radicals. This measure, however, is more suited to plasticizing of casting slips; extrusion batches generally have high-swelling colloids added, which do not lose their water under the high pressures in extrusion presses, and so ensure reliable flow of the batch from the die. Examples of such colloids are agar-agar or traganth (a vegetable mucilage, cf. WEBER) or starch paste well-steeped in H_2O plus some ammonia for several hours, or ethyl cellulose, such as Tylose, Ethoxose, Glutofix, and the like.

(c) A further difference between preparation of oxide and silicate ceramics is the far higher temperature of firing of the former (1800–2000°, in exceptional cases 2200°). The usual gas-fired chamber kilns of the ceramic industry are inadequate for this, and special gas-fired surface combustion furnaces are required. The basis for this is that in firing oxide ceramics with no melt additives (frits), densification (as already stated) occurs almost exclusively by recrystalization—in combination with grain-growth; that is, by migration in the solid (or gaseous?) state at high temperatures, rather than as a result of melting phenomena at relatively low temperature as with frit-bearing
[12.6] ceramics. This grain-growth can be influenced in the negative direction, but also in the positive, by adding various "mineralizers"; for example, traces of TiO_2 in alumina masses yields a dense, yet very coarse structure. The term "mineralizers" generally is understood to mean, certain additives, mostly in small amounts, made to ceramic batches, and which favor formation of definite *types* of crystal in the shard during firing; e.g. MgO or alkalis as mullite-formers in alumosilicates. Further, additives that influence grain-*size* in the shard are often called mineralizers.

By and large the following rule holds: the smaller the starting batch grains (i.e. the higher the surface energy), the faster and more easily does recrystalization occur, hence the larger the shrinkage and therefore the density attainable after the firing process is complete. (Purposely porous oxide ceramics therefore require coarser starting powder, and, obviously, lower firing temperatures.) The necessary firing schedule can be determined by measurements of shrinkage and mechanical strength of different high-fired test-pieces (see Fig. B 12-60B). Also, the value of modulus of elasticity of the fired piece is an indicator of the force that bonds the individual molecules (see Fig. B 12-60B again). In such investigations into consolidation processes by recrystalization, the most

TABLE T 12–25. TEMPERATURES OF ONSET OF FAST REACTION (2–8 min) IN THE SOLID STATE BETWEEN THE CHIEF REFRACTORY OXIDES AND CARBON IN CONTACT (JOHNSON, cf. also Table T 12–28)

	ONSET OF REACTION (°C) IN CONTACT WITH			
PARTNER I \ PARTNER II	C	ThO_2	BeO	ZrO_2
MgO	1800 (8)	2200 (4)	1800 (2)	2000 (4)
ZrO_2	1600 (4)	2200 (4)	1900 (2)	
BeO	2300 (2)	2100 (4)		
ThO_2	2000 (4)			

Numbers in ( ) = minutes elapsing before noticeable reaction occurs.

Further data (RYSCHKEWITSCH):

Al_2O_3—MgO strong reaction at 1600°
Al_2O_3—ZrO_2 reaction begins at *ca.* 1600°
Al_2O_3—C no reduction up to 2000°
Al_2O_3—H_2 no reduction up to 1900°
} see also Table T 12–28A

(DEGUSSA): Al_2O_3-Graphite in HV at above 1300°: not stable

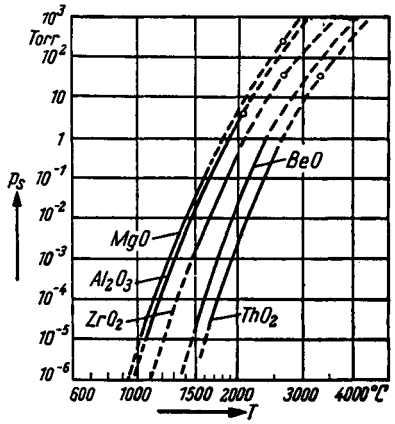


Fig. B 12-61 Saturation vapor pressure p_s of refractory oxides as functions of temperature T

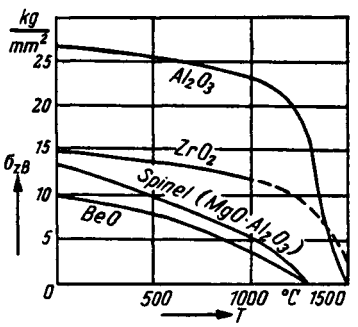


Fig. B 12-62 Tensile strength σ_{zB} of dense-sintered oxide ceramics as functions of temperature T ([1]RYSCHKEWITSCH)

[12.6]

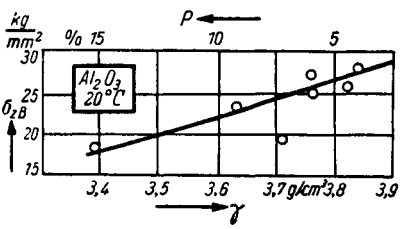


Fig. B 12-62A Tensile strength σ_{zB} of sintered alumina as functions of apparent density γ and porosity P (CUTLER)

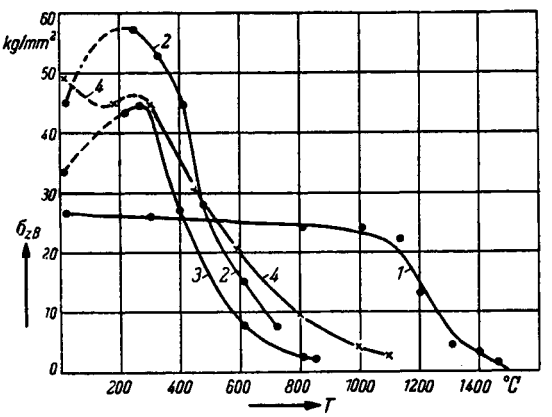


Fig. B 12-62B Tensile strength σ_{zB} of pure alumina ceramic as a function of temperature T and compared with various metals ([1]RYSCHKEWITSCH)

1 Al_2O_3; *2* mild steel (annealed at 700°); *3* ingot iron; *4* nickel

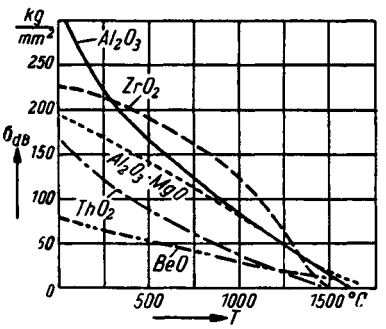


Fig. B 12-63 Compressive strength σ_{dB} of dense-sintered oxide ceramics as functions of temperature T ([1]RYSCHKEWITSCH)

TABLE T 12–26. PROPERTIES OF DENSE-SINTERED PURE-OXIDE CERAMICS ([1,2]RYSCH-

[12.6]

			Al_2O_3 [9]	MgO
Molecular weight			102	40
Density		g/cm³	3.79–3.87	3.39–3.57
Melting point		°C	(2015–) 2050	2800 (2672)
Max. temperature for use	in air	°C	1950	2400
	in vacuum		1800	1600 (–1700)
Temp. for vapor pressure	10^{-5} Torr	°C	1050	1040
	10^{-1} Torr		1640[15] [33]	1600[15]
Softening temp. under load (2 kg/cm²)[30]		°C	1860	2000
Tensile strength		kg/mm²	20 °C : 26.5[20] [28]	(980 °C : 2.2)
Compressive strength	20 °C	kg/mm²	300	(78)
	1600 °C		5[21]	–
Bend strength (20°C)		kg/mm²	33	–
Young's modulus		kg/mm²	20 °C : 34800[8] 38500[3]	20 °C : 3400–8900
			1250 °C : 24200 26200[3]	900 °C : 2860–7500
Torsions modulus[32]		kg/mm²	20 °C : 12000–17000 1550 °C : 3900–4100	20 °C : –
Mohs' hardness		–	9	5.5–6
Thermal expansion coefficient		10^{-7}/°C	25–1500 °C 96[12] [14]	25–1500 °C 160[12]
Thermal shock resistance			Very good	Poor
Thermal conductivity[19]		10^{-3} cal / cm s °C	20 °C : 47–90 1000 °C : ≈ 12[23] [27]	20 °C : ≈ 100 1000 °C : ≈ 15[23]
Specific heat	100 °C	cal / g °C	0.206	0.234
	1000 °C	cal / g °C	0.261	0.280
Electrical resistivity[18]		Ω-cm	1000 °C : 10^6–3 × 10^7	1000 °C : (1–3) × 10^5
			1600 °C : (1–5) × 10^3 [25]	1500 °C : ≈ 10^3 [25] [29]
Te value (10^6 Ω)		°C	1000–1200	830–900
Electrical breakdown strength		kV/cm	≈ 150 100–180[10]	
Dielectric constant ε		–	9.5–12	8–10
Dielectric loss angle tan δ		10^{-4}	5 × 10^7 c/s : 10–20	2 × 10^3 c/s : 800
Radiance	1227 °C	W/cm²	6.66	
	1727 °C		30.5	
Total emissivity		%	[26]	[26]
Reaction in contact with	W		>2000	2000
	Mo			1600
Price (approx.) in 1947[7]		$/lb	0.055	0.05

KEWITSCH, SALMANG, MICHAELSON, GANGLER, SABOL, [1]WHITTEMORE) *(Footnotes, see p. 566)*

$Al_2O_3 \cdot MgO$[2]	ZrO_2	ZrO_2 stab.[1]	BeO	ThO_2
	123		25	264
3.53–3.58	5.5–5.7	5.35–5.6 (1.8–4.4)	2.7 (–3.0)	9.6–10.0
2135	2700–2715	2550–2600	2550 ± 25	3000 (3300)
	2500		2200	2700
1800	1700		2000 (–2100)	>2300
	(10^{-3} : 1430)		1500[15] [16]	1600
	1820[15] [17]		2190[15] [16]	2300[15]
1600–1850	2000	1950	2000	≈ 2000
20 °C : 13.5 1300 °C : 0.8[20]	20 °C : 15–18 1500 °C : 1.3[20]	(980 °C : 4.7)	20 °C : 9.7 1300 °C : 0.45[20]	20 °C : 7–10.5 1000 °C : ≈ 7–10
173–190	210		80	150
6[21]	Soft[21]		5[21]	(1400 °C : 4)[21]
17	18	–	14	12.5[11]
20 °C : 22500	20 °C : 17500	(20 °C : 25200)	20 °C : 31000	20 °C : 14000
1250 °C : 8600	1250 °C : 11000		1250 °C : 11000	1170 °C : 8500
7800–7900	7100–7400	5000–5100[31]	10400	5800–6100
8	7[5] 8–8.5[6]	(7–8)	9	6.5–7
25–1500 °C 96[12]	Monoclinic: 25–1000 °C 65	Cubic: 25–1500 °C 116[12]	25–1400 °C 92–93.5 See. however[12]	25–1500 °C 104[12] [13]
Average	[4] Very poor	Poor	Very good	Poor
200 °C : ≈ 30 1000 °C : ≈ 13[23]	Low	100 °C : 4 2200 °C : ≈ 5.5[23]	140–> 200[23] [24]	100 °C : 20–24 1000 °C : 6–7[23]
0.194	0.120	20 °C : 0.120	0.299	0.06
0.257	0.157	(1500 °C : 0.175)	(900 °C : 0.497)	–
1000 °C : 10^5–10^6	1000 °C : 10^3–10^4	1000 °C : 10^2–10^3	1000 °C : 10^7–10^8	1050 °C : ≈ 10^4
1600 °C : 10^3–10^4[25]	2000 °C : 0.6[25]	2200 °C : 0.37[25]	2000 °C : 10^3–10^4[22] [25]	
≈ 800	400–570	–	1230–1320	–
9			7.5	17
2 × 10^9 c/s : 8			2 × 10^9 c/s : 3	2 × 10^9 c/s : 15
				9.23
				49.3
	[26]			[26]
–	1600	–	2000	2200
–	2200	–	1900	1900
–	0.9	–	4.0	7.0

[12.6]

FOOTNOTES TO TABLE T 12–26

(1) Composition of stabilized ZrO_2: 93% ZrO_2, 4.5–5% CaO, 1.5% HfO_2.

(2) $Al_2O_3 \cdot MgO$ = spinel = 72% Al_2O_3 + 28% MgO.

(3) Very pure alumina, see also Fig. B 12-60B.

(4) Because of transformation.

(5) Sintered ZrO_2.

[12.6]

(6) Fused ZrO_2.

(7) SABOL.

(8) Young's modulus of Al_2O_3: 1.3 mm dia., 31,000; 0.7 mm dia., 36,000; 0.3 mm dia., 43,200.

(9) Very pure but porous sintered Al_2O_3, see Table T 12–11, A1, No. 21 (Alsimag 548; porosity 14-17%).

(10) Measured in accordance with ASTM.

(11) ThO_2: impact bend strength = $3.3 \frac{kg \cdot cm}{cm^2}$.

(12) For T-dependence of α see Fig. B 12-64.

(13) See also LANG (ThO_2 + 0.5% CaO) and [2]CURTIS.

(14) See also WARDE.

(15) See also Fig. B 12-61.

(16) p_s values for BeO are unreliable: according to other measurements, the SVPs were more than an order of magnitude lower (e.g. 2080°: 1.8×10^{-3} Torr according to NORTON, 4260°: 760 Torr according to LONG).

(17) This value does not agree with JOHNSON's report that ZrO_2 and ThO_2 show no noticeable evaporation in vacuum up to 2300°.

(18) ϱ values depend strongly on degree of purity of the ceramic.

(19) Thermal conductivity values vary widely with porosity (apparent density), and therefore with temp. of firing and holding time. Cf. Fig. B 12-65A, see also KINGERY.

(20) For T-dependence of σ_{zB} see Figs. B 12-62 and B 12-62B.

(21) For T-dependence of σ_{dB} see Fig. B 12-63.

(22) See also RÖGENER.

(23) For T-dependence of λ see Fig. B 12-65.

(24) See Fig. B 12-66 for T-dependence of λ for BeO for various densities (degree of sintering).

(25) For T-dependence of ϱ see Fig. B 12-67.

(26) See Fig. B 12-68 for T-dependence of emissivity E_{rel}.

(27) See Fig. B 12-65A for porosity dependence of thermal conductivity λ for alumina.

(28) Tensiles depend strongly on apparent density γ (porosity P), see Fig. B 12-62A.

(29) See also DIEPSCHLAG.

(30) From [4]DIN 1064.

(31) Stabilized with 2.5 w/o MgO.

(32) [3]RYSCHKEWITSCH.

(33) According to measurements by BREWER, SVPs for alumina are much below the figures in Fig. B 12-61. The SVP curve therefore would lie roughly between those for BeO and ThO_2 in Fig. B 12-61.

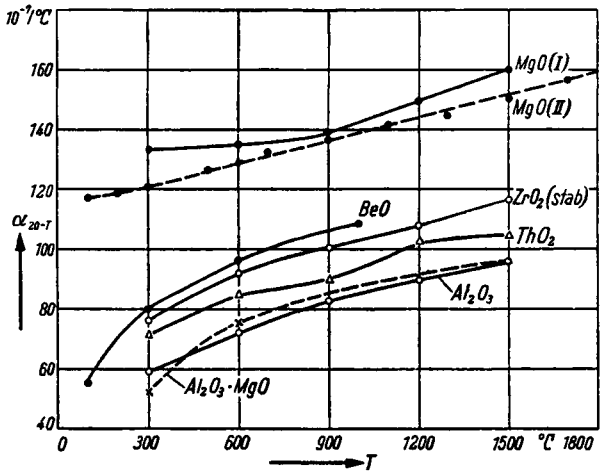


Fig. B 12-64 Mean linear thermal expansion coefficient $\alpha(20\text{–}T)$ between 20° and T °C, for various high-sintered oxide ceramics, as functions of temperature T

All curves except MgO (II) and BeO from [2]WHITTEMORE, BeO from UDY; see Fig. B 12-77 for expansion characteristic of stabilized ZrO_2

[12.6]

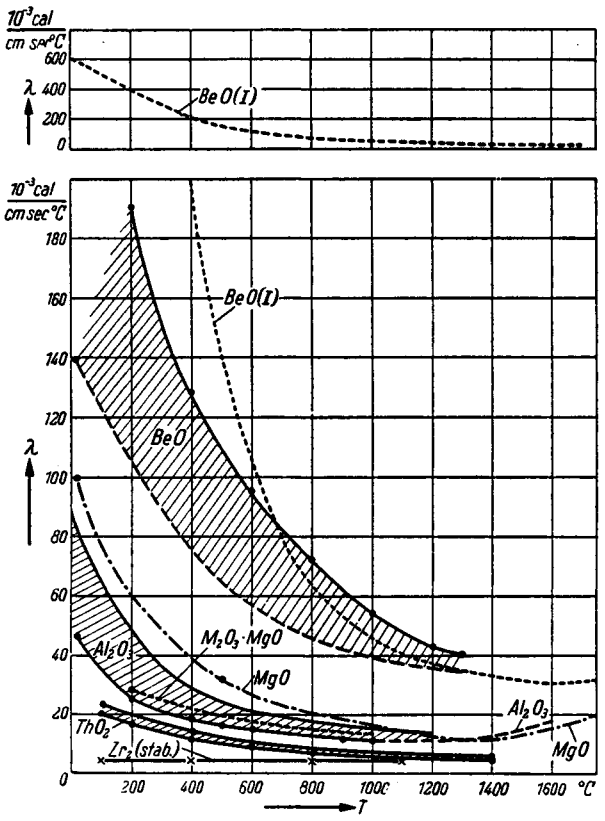


Fig. B 12-65 Thermal conductivity λ of various oxide ceramics as functions of temperature T[1] (see also [1]KINGERY)

BeO (I) from [1]FRANCL, MCQUARRIE; for BeO of various densities see also Fig. B 12-66, for porous Al_2O_3 see Fig. B 12-65A

[1] The fall in λ with rising temperature contrasts with the behavior of silicate ceramics where λ rises with T (see, e.g., Fig. B 12-16)

important result for technical purposes is that after exceeding a certain lower limit of temperature, corresponding increases in firing *time* can be substituted for inadequate temperatures, and this is true for all oxide ceramics.

[12.6]

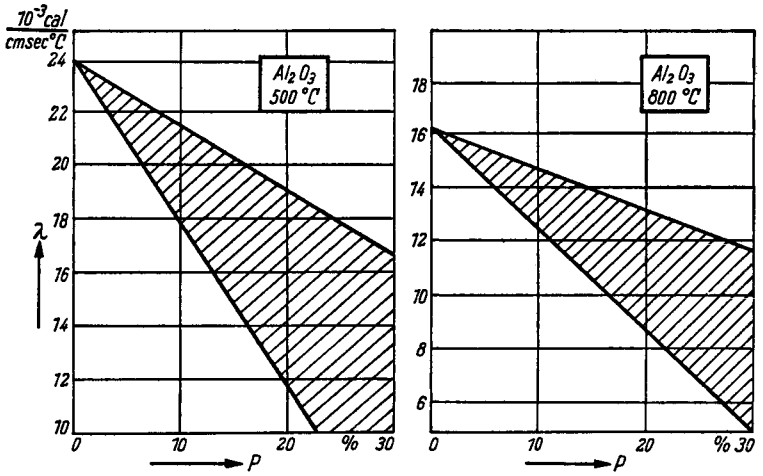


Fig. B 12-65A Thermal conductivity λ of various high-sintered aluminas at 500° and 800°, as functions of porosity P ([2]FRANCL)

(d) In firing oxide ceramics, special attention should be paid to seeing that no reactions occur between the furnace charge and the furnace walls, which themselves usually consist of oxides, since such reactions can lead to formation of low-melting eutectic

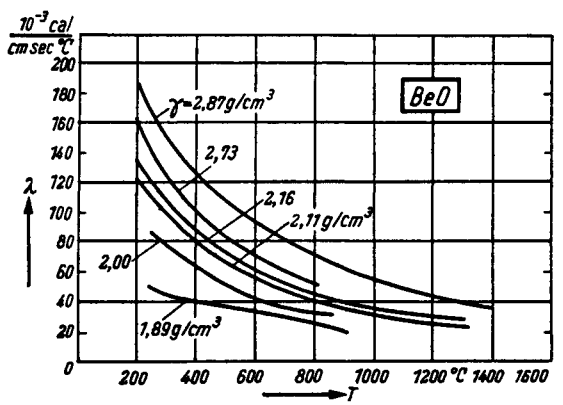
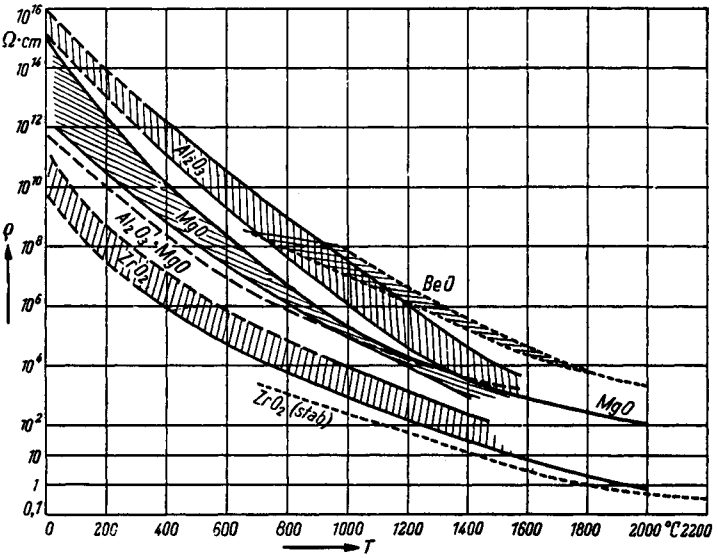


Fig. B 12-66 Thermal conductivity λ of BeO ceramics of differing density γ as functions of temperature T (UDY)

compounds. Table T 12–25 is of interest in this connexion; it contains the temperatures at which reactions start between the chief refractory oxides (and carbon) within a few minutes. It is best to select in each case bases on which the green ware rests, or components which suspend it, which are made of the same oxide as the ware itself. Since most

muffle furnaces for the temperatures involved here (up to 2000°) are made of MgO for reasons of economy, corresponding "inert" or "neutral" interlayers must be provided (see, e.g., Table T 12–32).



[12.6]

Fig. B 12-67 Electrical resistivity ϱ of various oxide ceramics as functions of temperature T. See also HELDT for measurement of resistance of pure alumina sintered in HV

The properties of pure oxides are tabulated in Table T 12–26 to permit comparison. This table is supplemented by a series of curves (Figs. B 12-61 to B 12-68), individually referred to in the table. Figure B 10-4 gives limiting value diagrams of tensile and

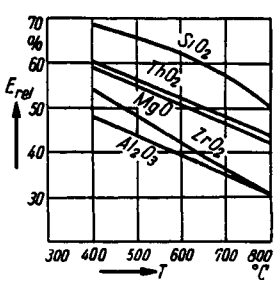


Fig. B 12-68 Total emissivity E_{rel}[1] of some pure oxides, sintered as powder on to heater strips, as functions of temperature T (SULLY)

[1] Total radiation from a black-body is set at 100%.

compressive strength for ceramics, including the oxides, and in comparison with glasses, metals, plastics, etc.; Fig. B 10-40 shows expansion coefficients, Fig. B 10-42 gives thermal conductivities and Fig. B 10-44 the electrical resistivities. A collection of the chief properties of some modern, commercial pure-oxide ceramics can be found in Table T 12–26 A.

TABLE T 12-26A. PROPERTIES OF A COMMERCIAL PURE-OXIDE CERAMIC (MADE BY DEGUSSA, DEGUSSIT DIVISION, FRANKFURT AM MAIN)

[12.6]

TRADE NAME "DEGUSSIT"			AL 23	AL 25	MG 25	SP 23	ZR 23	ZR 25
Composition		%	>99.5 Al_2O_3	>99.5 Al_2O_3	≈95 MgO, Rest Al_2O_3, Fe_2O_3, SiO_2	MgO · Al_2O_3	*ca.* 95 ZrO_2, rest: stabilizers	
Porosity		%	Dense[14]	Porous[15]	30	Dense	Dense	Porous
Density		g/cm³	3.7–3.9	3.0	≈ 2.5	3.3	5.4	4.5
Melting point		°C	2030		≈ 2500	≈ 2100	≈ 2500	
Working temperature		°C	max. ≈ 1900	max. 1900	max. 2300	1950	max. 2300	max. 2300
Tensile strength	20 °C	kg/mm²	26.5					
	1000 °C	kg/mm²	23					
Compressive strength	20 °C	kg/mm²	300					
	1000 °C	kg/mm²	85					
Refractoriness under compressive loading		°C	1730	1700		1900	2000	2000
Expansion coeff. (0–1000 °C)		$\frac{10^{-7}}{°C}$	83		130	90	115	
Thermal conductivity at 1000 °C		$\frac{10^{-3}\ cal}{cm\ s\ °C}$	12.5	8.3	≈ 7.2 (1600 °C: ≈ 5.5)	12.5	3.3–4.7	2.8
Total emissivity at 1060 °C		%	21		31	53	24	18
Electrical resistivity	1000 °C	Ω-cm	5×10^6			2×10^5	2×10^1	
	1500 °C	Ω-cm	1×10^4					
Dielectric constant 20 °C, 10^7 c/s			9.2			8	24	
Dielectric loss angle 20°C, 10^7 c/s			2×10^{-4}			$< 1 \times 10^{-4}$	20×10^{-4}	
Breakdown strength (electrical)	20 °C	kV_{eff}/mm	27					
	600 °C	kV_{eff}/mm	11					
Form supplied			[1] to [12]	[5] [6] [13]	[5] [6] [10] [13]	[7] [8] [9] [10]	[8] [9] [10]	[5] [7] [8] [13]

[1] Insulating sleeves (single or multiple capillaries).
[2] Insulating rod.
[3] Small insulating parts.
[4] Insulator blocks (Fig. B 12-69A) or bricks.
[5] Plates and rings.
[6] Powder as per Table T 12-30B.
[7] Grit (Fig. B 12-72A), sizes 0.1–20 mm.
[8] Open-ended tube.
[9] Tube closed at one end.
[10] Crucibles and boats.
[11] Mortars.
[12] Heater-wire fastenings (hooks, cylinders).
[13] Furnace segments.
[14] About 5% (*closed*) pores.
[15] About 25% (predominantly *open*) pores.

The following detailed comments should be made regarding the chief oxides:

12.6.I. *Pure Al_2O_3 Ceramics*

(GERDIEN, KOHL, [3]RUSSELL)

The starting material is alumina, obtained either by heating hydrated alumina at 1400–1500°, or obtained commercially as fine-crystalline powder made from arc-won corundum. It is ground in steel mills for 50–60 hr to 12–15 μ grain-size, at least 65% below 5 μ; the Fe is then removed by a magnetic separator followed by 24 hr in steam- [12.6] heated 10–15% HCl (200 liters for 100 kg Al_2O_3). Etching of grains and formation of oxychlorides (plasticizing, see above) takes place at the same time. The product is repeatedly washed with distilled water, but only until the acid concentration is 0.5%. 0.5% MgF_2 is often added to assist crystalization. Instead of HCl, tartaric acid may be added; this forms soluble Al-tartrate complexes which cement the grains of Al_2O_3. For extruded material, ethyl cellulose is added. Both are fed into the baked, ground batch (freed from Fe) through a fine sieve. Moldings are made by dry-pressing or extrusion, followed by thorough drying, or by isostatic compression in rubber molds.

Figure B 12-68A shows an example of isostatic molding equipment. A thin-walled rubber tube (*2*) is inserted in a brass tube (*1*), perforated peripherally. The ends of tube (*2*) are drawn back over the brass tube (*I*, *2a* and *2b*). Then (*II*) one end of the rubber tube and the brass tube are plugged with a cylindrical rubber stopper (*3*), and the folded end (*2a*) of the rubber tube is slipped over the stopper and tied with a wire coil (*6*). The inside of the rubber is now filled with powder (*5*). In (*III*), the upper opening of the tubes is sealed with a rubber stopper, which, unlike (*3*), has a shoulder to prevent it sliding into the tube during pressurization and so facilitate subsequent removal of the finished molding. A hypodermic needle and thick-walled rubber connecting-hose (*7* and *8*) are used to extract the air from the powder. After careful removal of the needle (*IV*), the end (*2b*) of the rubber tube is drawn over the upper stopper (*4*) and closed off with a wire twist (*9*). The whole device is inserted in a hydraulic pressure vessel and the powder subjected to hydrostatic pressure of about 2.5 ton/cm^2 by means of the pressure fluid through the perforations in the brass tube and via the stopper (*3*) which can slide upwards. The powder is thus compressed isostatically to a solid compact.

The alumina body is fired either in a Mo-wound hydrogen stove or in the oxidizing atmosphere of a gas-fired surface combustion furnace, using city gas of at least 4000 kcal/standard m^3, composed of about 50 v/o H_2, 20 v/o CH_4, 15 v/o CO, etc. The sintering furnace is usually lined with electrically fused pure MgO. Sintering time generally amounts to 1–3 hr at 1700–1940°; the small corundum crystals of the starting batch grow to larger aggregates and perhaps there is some "cementing" by overheated and therefore melted alumina particles. Densification ensues with a volume shrinkage of 20–40%, so that no capillaries remain between the individual crystals of the so-called "sintered corundum". The internal porosity that remains (gas inclusions of 1–2 μ inside the crystals) can be reduced to 2–4% by sufficiently high firing temperatures and adequate holding times. Figure B 12-68B shows a section of an alumina ceramic fired at 1710° with only 0.2–0.5% impurity. If, instead of starting with pure alumina, the material

is allowed to have small amounts (*ca.* 2%) of other constituents from the original mineral (e.g. CaO, MgO, Fe_2O_3), such "mineralizers" do indeed assist the sintering process, but the grains are larger than with pure alumina as is shown by comparing

[12.6]

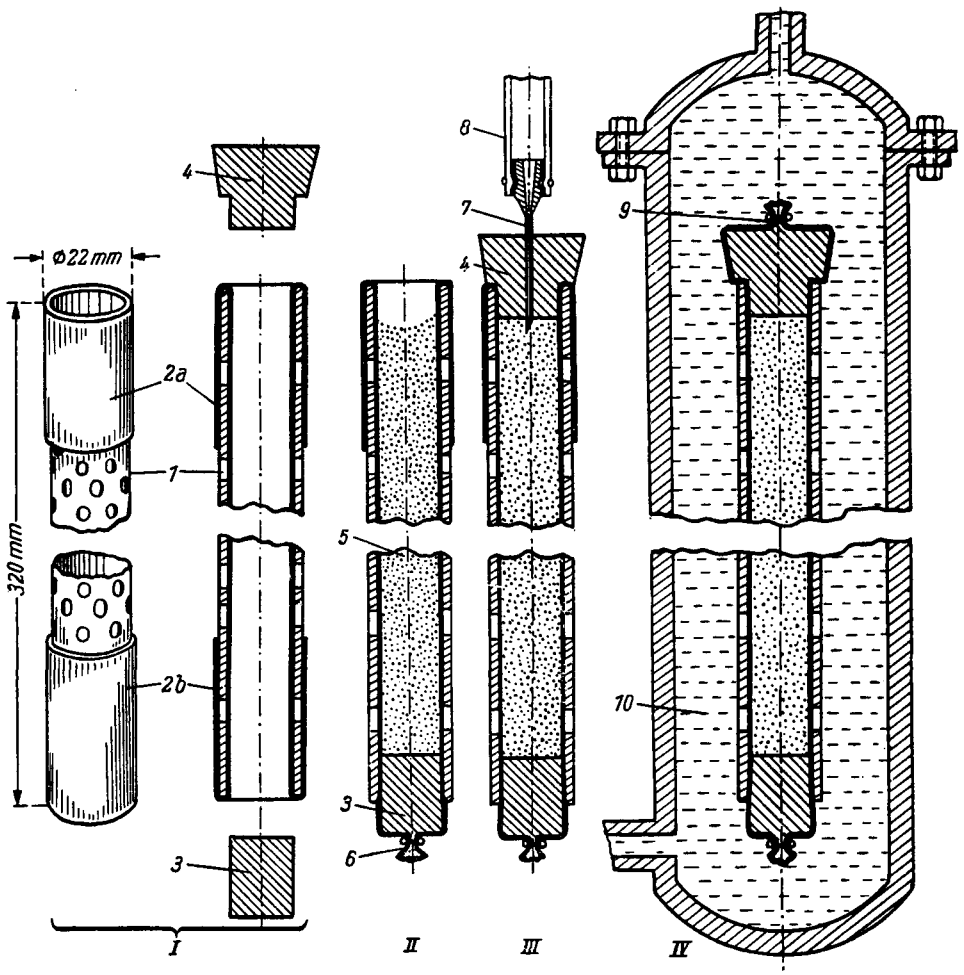


Fig. B 12-68A Example of a hydro-(iso)-static press for molding ceramics from dry powder and corresponding stages in the procedure (BLACKBURN)

1 brass tube (22 mm dia., 320 mm long) with a large number of peripheral holes (6 mm dia.); *2* thin-walled rubber tube with ends *2a* and *2b* folded back over outside of tube *1*; *3* cylindrical rubber bung; *4* rubber bung with shoulder; *5* compressed powder; *6* end of rubber tube *2* closed with wire wrap; *7* hypodermic needle inserted into thick-walled vacuum-rubber tube *8*; *9* as *6*; *10* hydraulic press

sections of sintered corundum in Figs. B 12-68B and B 12-68C, both of which had about the same firing temperature and holding time.

Besides these dense-sintered corundum ceramics, *porous* aluminas can be made for special purposes; they have a water absorption of 10–17%, and a density of 2.4 g/cm³

instead of 3.84 (see, e.g., Table T 12–10, A 1, no. 21, Alsimag 548). Table T 12–27 contains a simple recipe for making porous alumina insulator rods for supporting cathode filaments.

Clearly, in dense-sintering alumina ceramics, the firing temperature can be lowered to 1500–1650° by addition of silicate-bearing materials (Al-silicate, ground soapstone or talcum) which form cementing mullite melts ($3\ Al_2O_3 \cdot 2\ SiO_2$). This cuts the costs of firing. However, it involves changing from the preparation of a *pure* oxide to that of a high-alumina *silicate* ceramic, with a corresponding decrease in the maximum permissible operating temperature (see Fig. B 12-69). Pure sintered alumina contains as a [12.6]

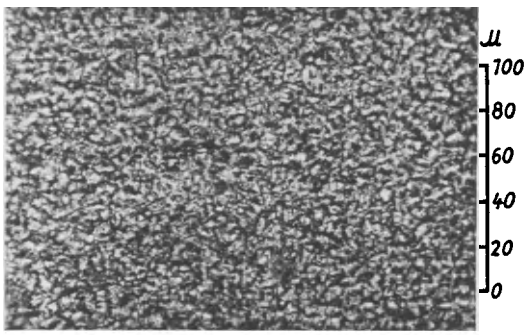


Fig. B 12-68B Sintered corundum (99.5 to 99.8% Al_2O_3); photograph of thin section taken by ordinary transmitted light, mag. × 500 (VÚEK)

Batch milled for 50 hr in ball-mill with sintered corundum balls and milling ratio[1] 1 : 1 : 1, overall firing time 8 br, at 1710° max. (about 10 min holding time), fine-grain structure; cf. also Fig. B 12-39 C

[1] ratio = parts by weight of batch to parts by weight of water to parts by weight of balls

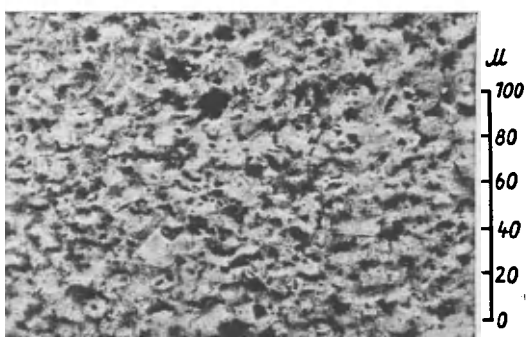


Fig. B 12-68C Sintered corundum, about 98% Al_2O_3 + mineralizers (CaO, MgO, Fe_2O_3); thin section photographed by ordinary transmitted light, mag. × 500 (VÚEK)

Milled as in Fig. B 12-68B, overall firing time 8 hr, firing temperature 1700° (10 min holding time). Mineralizers assist sintering but produce large grains compared with those from pure alumina batches

rule at most 0.1% Fe_2O_3, 0.1% MgO and 0.2% CaO. Many commercial aluminas of the type DIN 610 (see Table T 12–11 D) contain 2.0–2.5% Cr_2O_3 to increase hardness ([3]RUSSELL).

Pore-free sintered pure alumina is far removed from glasses and silicate ceramics in characteristics, because of its purely crystalline structure. It has above all a very high thermal conductivity (Fig. B 12-65), which can be up to 20 times higher than that of hard porcelain; however, λ together with mechanical strength fall, as porosity rises, as would be expected (Fig. B 12-62 A).

The electrical resistivity of sintered alumina is high even at elevated temperatures and, other things being equal, is higher for porous material than for dense-sintered. Electrical losses are low, especially for pure alumina. In thin-wall sections, sintered corundum

(dense-sintered Al_2O_3) is quite translucent. It is also impermeable to fluids and gases, in the ordinary sense of the word ([1]RYSCHKEWITSCH), but permeability to H_2 at elevated temperatures even of very high-sintered alumina is often larger than that of

[12.6]

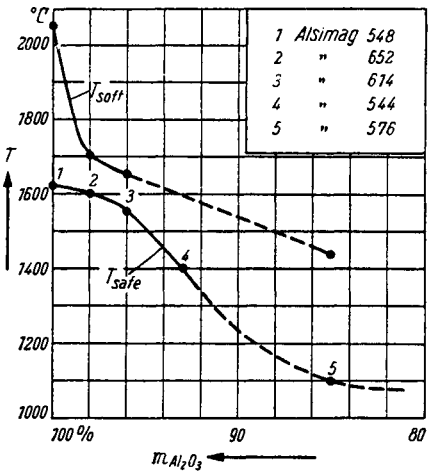
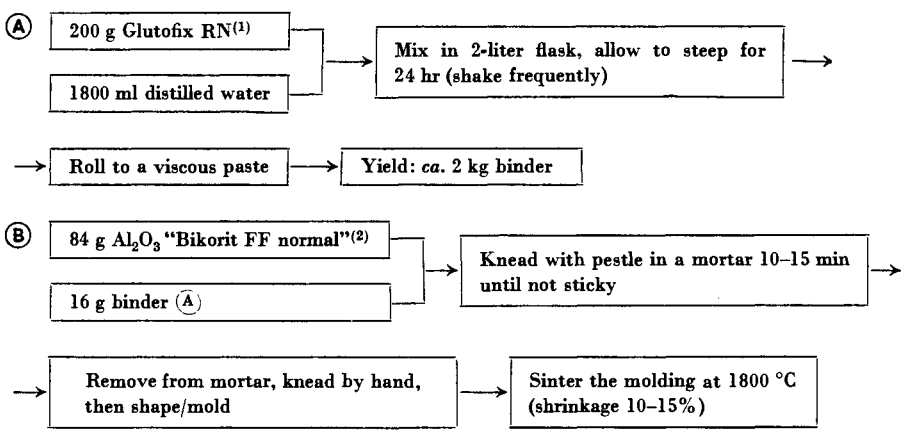


Fig. B 12-69 Softening point T_{soft} and maximum permissible working temperature T_{safe} of commercial, sintered-alumina-type ceramics, as functions of alumina content $m_{Al_2O_3}$

porcelain (cf. Table T 12–14); this is apparently explicable by the purely crystalline structure, devoid of glassy binder, which permits unhindered migration of gas along the grain-boundaries. Sintered alumina is very stable in an oxidizing or neutral atmosphere;

TABLE T 12-27. MANUFACTURE OF ALUMINA RODS


Ⓐ
200 g Glutofix RN(1)
1800 ml distilled water
Mix in 2-liter flask, allow to steep for 24 hr (shake frequently)
Roll to a viscous paste
Yield: ca. 2 kg binder
Ⓑ
84 g Al_2O_3 "Bikorit FF normal"(2)
16 g binder (A)
Knead with pestle in a mortar 10–15 min until not sticky
Remove from mortar, knead by hand, then shape/mold
Sinter the molding at 1800 °C (shrinkage 10–15%)

(1) Methyl cellulose-ethyl cellulose mixture, sold by KALLE UND CO., Wiesbaden.
(2) Sold by FELDMÜHLE-PAPIER U. ZELLSTOFFWERKE, Köln-Lülsdorf.

H_2 has no effect up to 1900°; it is virtually unattacked by HF because of the absence of SiO_2 content, but is attacked by alkali fluorides, H_2SO_4, alkalis, alkali earths and molten acidic sulphates. It is important to note that alumina in contact with SiC (with

TABLE T 12–28. MAXIMUM WORKING TEMPERATURE T_{max} OF PURE-OXIDE CERAMICS IN CONTACT WITH VARIOUS HIGH-TEMPERATURE HEATER MATERIALS, IN COMPARISON WITH OTHER FURNACE MATERIALS (KIEFFER)[7]

OXIDE	T_{max} (°C) IN CONTACT WITH				
	W	Mo	Ta	$MoSi_2$	C [6]
Al_2O_3	1900	1900	1900[8]	1400	2000
MgO	2000[1]	1800[2]	1800	1400	1800
ZrO_2	1600[2]	1900[2][3]	1600	1400	1600
BeO	2000[2]	1900[2]	1600	1400	2300
ThO_2	2200[2]	1900[2]	1900	1400	2000
Other materials	(for comparison)				
Graphite	1400[4]	1200[4]	1000[4]	1500[5]	–
Sillimanite brick	≈ 1700	≈ 1700	≈ 1600	≈ 1400	–
Magnesite brick	≈ 1600	≈ 1600	≈ 1500	≈ 1400	–
Firebrick	≈ 1200	≈ 1200	≈ 1200	≈ 1100	–

[12.6]

[1] Intense evaporation of MgO in high vacuum; in reducing atmosphere only usable to 1600°.
[2] In vacuum better than 10^{-4} Torr; in a reducing atmosphere a T_{max} of only 100–200° less is possible.
[3] Intense Mo evaporation.
[4] Onset of rapid carbide formation.
[5] Onset of rapid C take-up.
[6] JOHNSON's data; see Tables T 12–25 and T 9.2–2.
[7] Cf. also Table T 12–25.
[8] This is apparently too high according to recent measurements by [3]NAVIAS.

O_2 excluded) is inert up to 1900°, and is not reduced by graphite, W or Mo up to 2000°; this means that W or Mo heaters for construction of electric furnaces, and directly wound on sintered alumina (pure oxide) supports, can go up to 1900° without difficulty in HV or protective atmospheres such as forming gas (75% N_2 + 25% H_2, ammonia gas, or pure H_2) (see Tables T 12–28, T 12–28A). In hot arcs, pure Al_2O_3 goes grainy and brittle.

Applications of alumina ceramics in vacuum technology. Sintered alumina is a relatively cheap ceramic even when high-sintered, though to a lesser extent than MgO. When rough and highly porous (water absorption = 14–17%, as per Table T 12–11, A1, no. 21), it is readily degassed and is therefore used in transmitter-tube constructions, to run at very high working temperatures as distance pieces and insulators (also as disks up to 0.7 mm thick, see Fig. B 12-50). However, finish grinding to the exact tolerances needed for these purposes is made difficult by the great hardness of the material.

In the dense-sintered state, alumina is used for tubing (usually 150 cm long and 12 cm dia.) or for insulator bricks (Fig. B 12-69A) for vacuum and protective-atmosphere furnaces in direct contact with furnace windings of NiCr, Pt, Mo, W, etc. Examples:

(a) H_2 degassing furnaces up to 1500–1800° with sintered corundum tube muffle (Fig. B 9.2-16 IV, No. 1); a special example of a hydrogen furnace for use up to 1800°

TABLE T 12-28A. BEHAVIOR OF PURE SINTERED ALUMINA CRUCIBLES IN CONTACT WITH OTHER MATERIALS, AT ELEVATED TEMPERATURES ([2,3]JAEGER; CF. ALSO TABLES T 12-25 AND T 12-28)

REACTION WITH	FURNACE		REACTION
	TEMP. (°C)	ATMOSPHERE	
Al	700	H_2	None
Ba	*ca.* 1000	Vacuum	None up to evaporation point of Ba
[12.6] Be	1400	He	None, also none in vacuum ($<10^{-3}$ Torr)
	1600	He	None, also none in vacuum ($<10^{-3}$ Torr)
	1800	He	Weak reaction, formation of $BeO \cdot Al_2O_3$
H_2	Up to 2000	–	No reduction, but slightly impure alumina with reducible impurities at grain-boundaries shows weakening of crystal-crystal bonds and fall in strength
Fe	1600	H_2	None
Mn	1250	H_2	None
Mo	1400–1800	He	None
Nb	1400	He	None
	1600	He	
	1800	He	Weak reaction, formation of Nb_2O_3
Ni	1400–1800	He	None
Pd	1500–1650	Air	None
	1200	H_2	Attack by Pd-catalyzed H_2
Pt[1]	1800	Protect. atm.	None if alumina very pure (Fe-free)
Se	High	Vacuum	None
Si	1400	He	Weak reaction, formation of $SiO_2 \cdot 3\,Al_2O_3 \cdot 2\,SiO_2$
	1600	He	Strong reaction, formation of $SiO_2 \cdot 3\,Al_2O_3 \cdot 2\,SiO_2$
Ti	1400	He	None
	1600	He	Weak, formation of TiO_2
	1800	He	Strong
U	1200	Vacuum	None
W	1900	Vacuum	No reduction

[1] CaO crucibles preferred for melting down Pt (see 4.1).

TABLE T 12-28A *(continued)*

REACTION WITH	FURNACE		REACTION
	TEMP. (°C)	ATMOSPHERE	
Zr	1400	He	None
	1600	He	Weak } reaction, formation of ZrO_2
	1800	He	Strong } reaction, formation of ZrO_2
$Al_2O_3 \cdot MgO$ (spinel)	1900	Gas furnace	Very weak
BeO	1900	Gas furnace	Some reaction
MgO	1900	Gas furnace	Spinel formation, only at alumina surface
ThO_2	1900	Gas furnace	Reaction
ZrO_2	1900	Gas furnace	Strong reaction

[12.6]

with an alundum tube is shown in Fig. B 12-70. It is recommended in the interests of long furnace life not to raise the temperature faster than 100°/hr and in continuous operation never to let it fall below 1000–1200°.

(b) HV degassing furnaces with Mo windings, up to 1500° (Fig. B 9.2-9A).

(c) Graphite-tube, resistance-heated furnaces with gas-tight inner tubes (Fig. B 8.5-27).

Further examples of applications: insulators for Mo radiation heaters in vacuum furnaces (Fig. B 3.3-11); insulator rods for W or Mo windings in furnaces of the type shown in Fig. B 9.2-16, VI (No. 1). Supports in the form of mandrels (rods) and sleeves for W cathode filaments; the commercially guaranteed dimensional tolerances are given in Table T 12-29.

TABLE T 12–29. COMMERCIALLY GUARANTEED TOLERANCES AND MINIMUM DIAMETERS OF CATHODE FILAMENT CORES MADE OF SINTERED CORUNDUM DIN TYPE 710 (PORZELLANWERKE NEUHAUS)[1]

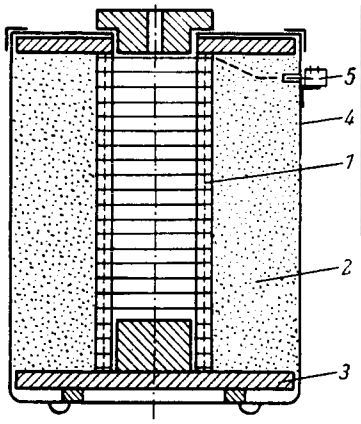
NOMINAL DIAMETER (mm)	TOLERANCE (mm)	FORM	MINIMUM DIAMETER (mm)
Up to 0.5	+0.02	Cores (rods)	0.25
Up to 1	+0.04	Sleeves outer	0.5
Up to 2	+0.06	inner	0.2

[1] Insulation satisfactory up to 1750° when used for W filaments.

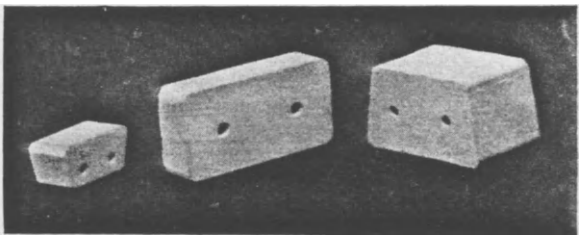
Insulating sleeves for W filaments were used very frequently before 1935 for I.H. oxide cathodes (Figs. B 12-71, B 12-72); requirements for tolerances on O.D. and on bores (numbering up to 5 in a 1–2 mm O.D. alumina sleeve) were very stiff. Today, this construction has given place almost completely to an alumina powder layer sintered directly on the W heater wire in a protective gas (see below).

Melting crucibles, e.g. for protective atmosphere and vacuum furnaces (see Fig. B 9.2-3, III, or Fig. B 6.1-17, 2) for ferrous and non-ferrous alloys, Ni, Cu. Also for

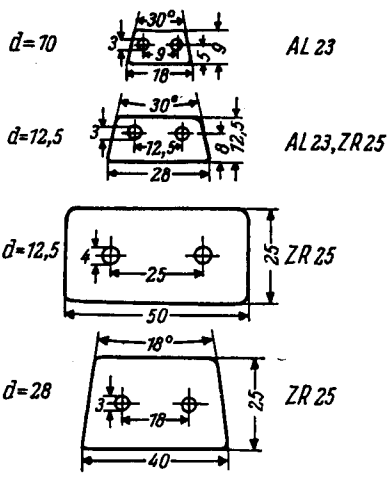
[12.6]



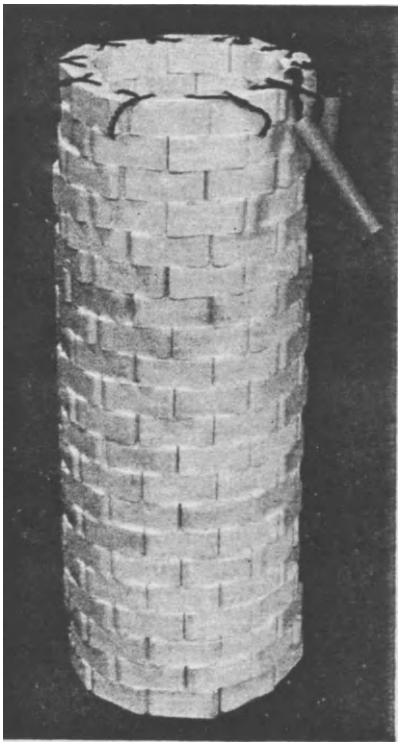
I



III



II



IV

Fig. B 12-69A Electric high-temperature protective-atmosphere furnace for use up to 1900°; working space 75 mm dia., 270 mm high; Mo heater wire threaded through Al_2O_3 or ZrO_2 insulating blocks made of Degussit AL 23 or Degussit ZR 25 (courtesy of DEGUSSA, Frankfurt am Main)

I furnace construction: *1* insulating blocks (210 off) threaded over 5.5 m of heater wire; *2* insulating grit (6 kg) of porous sintered alumina, Degussit AL 66, 5–10 mm dia. (Fig. B 127-2A); *3* baseplate of kaolin-bonded corundum, Degussit K 25; *4* housing made of 1–2 mm sheet iron; *5* current lead-in

II dimensions of brick insulators (blocks) in mm, d = thickness

III view of insulators

IV view of assembled heater unit

40 times dearer than ordinary technical-grade electro-corundum, and sapphire "pears" are 80 times dearer. The starting material must be comminuted to 5 μ at least to avoid too rapid sedimentation of alumina in the suspension during cataphoresis. This is a difficult and prolonged process because of the hardness of the corundum, but at all costs the entrainment of alkali-bearing impurities, such as would come from the lining of an ordinary porcelain ball-mill, must be avoided. For this reason the preference in practice is often to use iron ball-mills, and the Fe entrained and ground into the mill-batch is dissolved out with acid, whose residue is carefully washed away.

[12.6]

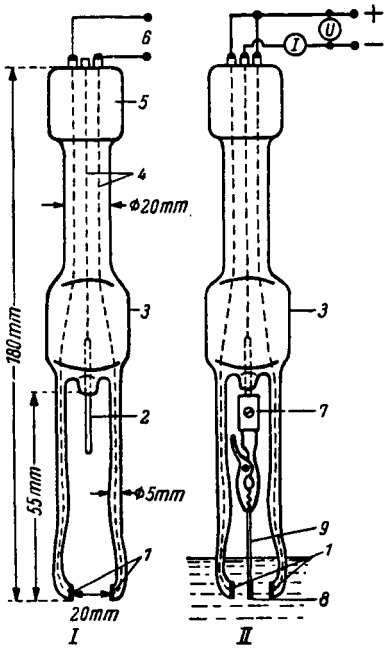


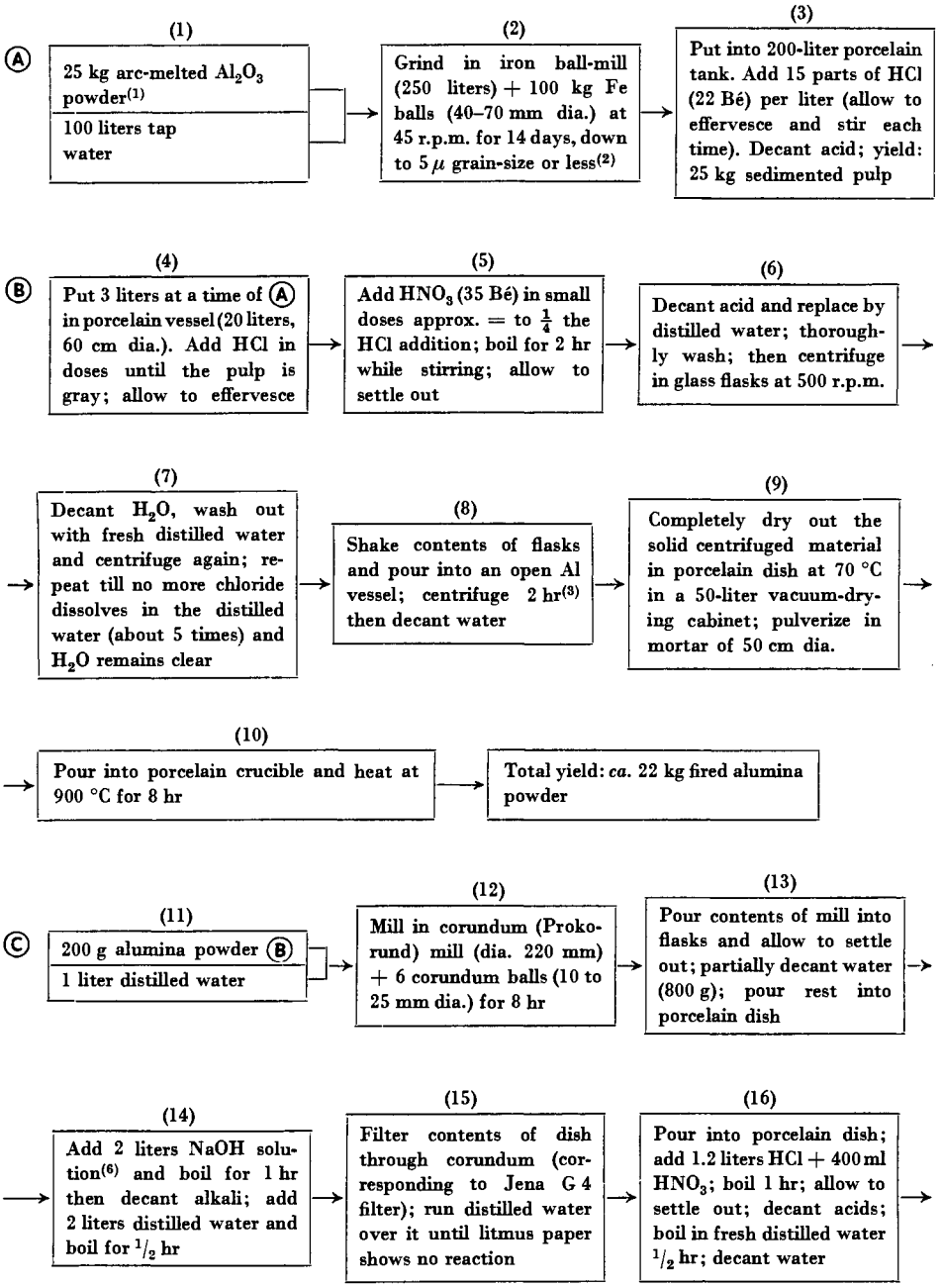
Fig. B 12-73 Probe for measuring resistivity of fluids (I) and for determination of the cataphoretic properties of alumina suspensions (II)

1 Pt wafers, each 1 cm² area, sealed liquid-tight to the ends of glass tubes; *2* FeCr (75/25) wire 1.25 mm dia. sealed into glass; *3* glass tube; *4* Cu lead-wires; *5* holder; *6* connexions to resistance bridge; *7* stainless steel clip; *8* Ni sleeve 3 mm O.D. with ends sealed-off by welding; *9* support wire 0.1 mm dia., of Ni (see also Chapter 24 for discussion of II)

The process given in Table T 12–30, an example of a particularly careful method of preparation, is based on the foregoing points. The purity of the auxiliary fluids is best controlled by determination of electrical resistivity, using an immersion probe; Fig. B 12-73 (I) shows a type well-proved in practice. The purity demanded of the corundum powder produced is obviously specially high in the preparation of I.H. "high-voltage" cathodes where the operating voltage of the filament is over 50 V, and the cathode-forming voltage is as high as 120 V. This is also true of cathodes where, for reasons of circuitry, up to about 250 V is applied between filament and Ni sleeve; in this case the peak permissible leakage current across the two should not exceed 20 μA, when the alumina coating is 70–100 μ thick, the temperature of the electron-emitting oxide layer is 730–750° and that of the W filament is about 1130°. The insulation resistance of the alumina coating must therefore be of the order of $10^7\,\Omega$. For such purposes the Al_2O_3 powder must have an alkali oxide content less than 0.02% and an Fe_2O_3 content less than 0.1%, while the SiO_2 content for a sintering temperature of 1650° (corresponding

TABLE T 12-30. A PREPARATORY PROCESS FOR ALUMINA INSULATION POWDER FOR SINTERING ON TO CATHODE FILAMENTS

[12.6]


(A)
(1)
25 kg arc-melted Al_2O_3 powder(1)
100 liters tap water
(2)
Grind in iron ball-mill (250 liters) + 100 kg Fe balls (40–70 mm dia.) at 45 r.p.m. for 14 days, down to 5 μ grain-size or less(2)
(3)
Put into 200-liter porcelain tank. Add 15 parts of HCl (22 Bé) per liter (allow to effervesce and stir each time). Decant acid; yield: 25 kg sedimented pulp
(B)
(4)
Put 3 liters at a time of (A) in porcelain vessel (20 liters, 60 cm dia.). Add HCl in doses until the pulp is gray; allow to effervesce
(5)
Add HNO_3 (35 Bé) in small doses approx. = to ¼ the HCl addition; boil for 2 hr while stirring; allow to settle out
(6)
Decant acid and replace by distilled water; thoroughly wash; then centrifuge in glass flasks at 500 r.p.m.
(7)
Decant H_2O, wash out with fresh distilled water and centrifuge again; repeat till no more chloride dissolves in the distilled water (about 5 times) and H_2O remains clear
(8)
Shake contents of flasks and pour into an open Al vessel; centrifuge 2 hr(3) then decant water
(9)
Completely dry out the solid centrifuged material in porcelain dish at 70 °C in a 50-liter vacuum-drying cabinet; pulverize in mortar of 50 cm dia.
(10)
Pour into porcelain crucible and heat at 900 °C for 8 hr
Total yield: ca. 22 kg fired alumina powder
(C)
(11)
200 g alumina powder (B)
1 liter distilled water
(12)
Mill in corundum (Prokorund) mill (dia. 220 mm) + 6 corundum balls (10 to 25 mm dia.) for 8 hr
(13)
Pour contents of mill into flasks and allow to settle out; partially decant water (800 g); pour rest into porcelain dish
(14)
Add 2 liters NaOH solution(6) and boil for 1 hr then decant alkali; add 2 liters distilled water and boil for ½ hr
(15)
Filter contents of dish through corundum (corresponding to Jena G 4 filter); run distilled water over it until litmus paper shows no reaction
(16)
Pour into porcelain dish; add 1.2 liters HCl + 400 ml HNO_3; boil 1 hr; allow to settle out; decant acids; boil in fresh distilled water ½ hr; decant water

metals with a great affinity for O_2, such as alkali earths, alkali metals (perhaps with the exception of Li), Si, Al, Th, etc.

Porous alundum crucibles for electrolytic purification of Hg as per Fig. B 8.4-2c, 4.

Granular alumina, today commercially available in various grain-sizes, grades of purity and apparent density (see, e.g., [1]ANON.), as is the case for MgO and stabilized [12.6]

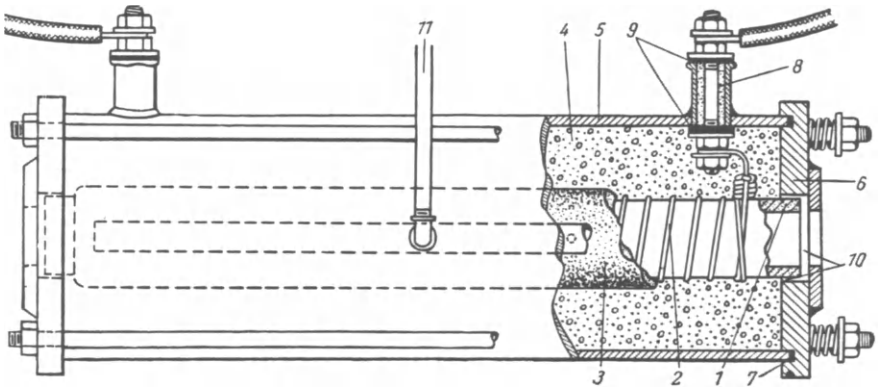


Fig. B 12-70 Hydrogen furnace (5–10 kVA) with Mo heater winding and muffle made of dense-sintered Al_2O_3 ("alundum") tube, for use up to 1850° (KEITH)

1 alundum tube *ca.* 60 cm long, 10 cm dia.; *2* soft-annealed Mo wire 1–2 mm dia. (or two twisted wires), 60 turns 7–10 mm apart, wound directly on to the tube *1*, but stood slightly off because the α of Mo is less than that of Al_2O_3, specific heater rating max. 0.7–1 W/mm² of heater surface, max. voltage 2–2.5 V per turn, i.e. about 120 V for the 60 turns; *3* alumina paste plus binder applied 3–5 mm thick to hold the Mo turns; *4* thermal insulation of granular alumina; *5* gas-tight outer tube of Fe; *6* steel end-plates; *7* asbestos gasket; *8* asbestos insulator tube; *9* insulating disks of mica; *10* expansion clearance between alundum tube and steel components; *11* H_2 inlet and outlet tubes

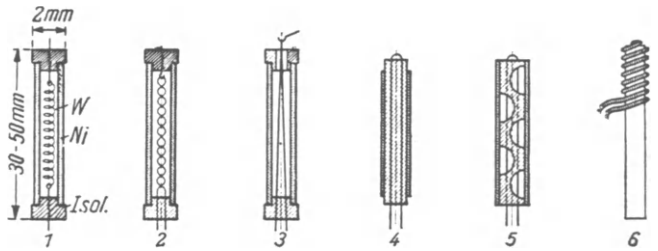


Fig. B 12-71 Examples of the construction of I.H. cathodes with alumina insulating sleeves

1 to *3* radiation heated; *4* heating by thermal conduction; *5* to *6* combined radiation and conduction heating; *1* to *5* with high-fired alumina insulator tubes (*5* with low heat capacity and hence rapid heating); *6* with mandrel of alumina rod, with W coil + sprayed/sintered insulator (for higher heater voltage, the equipotential cylinder is omitted)

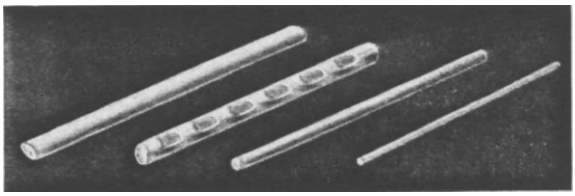


Fig. B 12-72 Types of alumina sleeves for I.H. cathodes: lengths 30 mm, dia. 5 to 2 mm from left to right of the figure (made by STUPAKOFF LABORATORIES INC.)

ZrO_2; it is used for thermal insulation of high-temperature furnaces (see, e.g., Fig. B 12-70, No. 4), and it should be noted that as apparent density falls so does thermal conductivity and hence the insulating properties of the alumina increase.

Figure B 12-72A shows alumina insulation material of this type made from highly-porous sintered Al_2O_3 (99.5%) with 60–80% porosity; it is a commercial product.

Alumina powder for insulating heater elements in I.H. oxide cathodes. A particularly careful manufacturing technique is required for the types of powder used for W filaments. Essentially, the process is one of cataphoretic deposition of thin layers of alumina
[12.6] from powder suspensions, or spraying the layer directly on to the cathode filament, followed by sintering to the substrate in a protective gas furnace at 1500–1700°, or by direct heating of the W by passage of current. The full details are given in Chapter 24

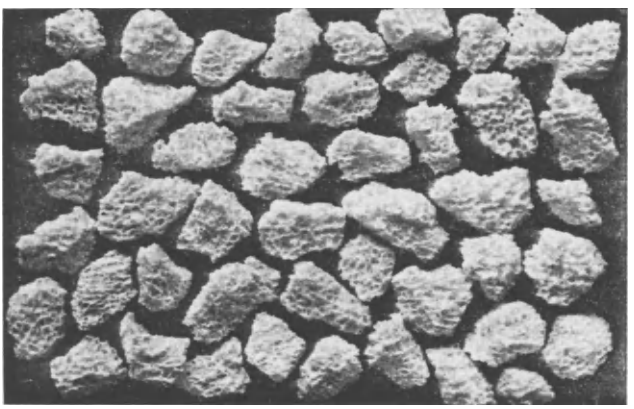


Fig. B 12-72A High-porosity sintered alumina grains, "Degussit AL 66", used as a thermally and electrically insulating filler for high-temperature furnaces (made by DEGUSSA, Frankfurt am Main)

(section entitled "Manufacture of indirectly heated oxide cathodes"); at this point only the preparation of the alumina powder is dealt with.

Since very high standards of insulation resistance are set for sintered alumina coatings, the powder and all auxiliary materials used in its preparation must be of highest controllable purity, above all alkali-free. The spray process involves high wastage of suspension so that, more recently, cataphoretic methods of coating have become preferred. Suspensions for this must be made from particles of crystalline alumina since only they have cataphoretic properties. The starting material is therefore mostly alkali-free alumina, arc-melted twice and crystalized from the melt, i.e. α-corundum; obviously, this material must be freed from residual carbon from the arc electrodes. It can be obtained from manufacturers of abrasives in grain-sizes from about 50 to 500 μ. Another material that can very well be used as a starting material is synthetic sapphire, which is generally made from highest possible purity alumina precipitated from ammonium-alumina-alum in an oxyhydrogen blow-flame ("Verneuil furnace") (see, e.g., BARTH-VUILLEUMIER, [1,2]KAŠPAR, ULLMANN). This is referred to below, see especially Table T 12–30A. However, it is much more expensive; in fact, sapphire powder is about

TABLE T 12-30 *(continued)*

(17) Filter through G 4 filter, wash with hot distilled water till neutral reaction →

(18) Testing: shake powder with methanol of $\varrho = 450\,k\Omega$-cm; the resistivity of methanol should not be appreciably lower than before[5] →

(19) When alumina powder settled out, and supernatant decanted, dry in vacuum-drier[4] for 2 hr at 100 °C; pulverize in porcelain dish and sieve through sieve-shaker (160–240 mesh/cm); pour into glass flasks →

Overall yield: *ca.* 20 kg very pure alumina powder ($\leqq 5\,\mu$)[6] [12.6]

(1) Max. grain-size about 200 μ (see Table T 12–30A, No. 1).
(2) Inspection by microscope, 800–1000 mag. power.
(3) Centrifuge 200–1500 r.p.m.; capacity for at least 3 kg solid material.
(4) Vacuum drier 50 liters/min pumping speed up to 150 °C with two pumps.
(5) Suspension must show cataphoretic properties.
(6) Consumption of reagents per kg very pure alumina: 250 g NaOH, 2.5 liters HNO_3, 7.75 liters HCl.

to less than 3% shrinkage) amounts to roughly 0.1%. If the powder is quite silica-free the sintering temperature lies above 1700° (see Fig. B 12-74); this causes intensive recrystalization of the underlying W wire and the alumina-coated filament has a high breakage rate in mounting. A certain amount of silica is therefore permitted in the alumina employed but experience shows that it should not exceed 0.3% or the insula-

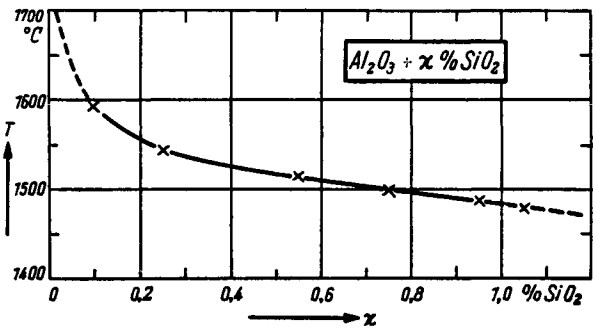


Fig. B 12-74 Required temperature T for sintering adherent alumina layers on W wires in 10–20 min, as a function of SiO_2 content (HORÁČEK)

tion resistance of the sintered coating drops too much. This admixture of SiO_2 can be made by a final grinding of the alumina powder in a Prokorund mill (see No. 12 of Table T 12–30). Since Prokorund (Table T 12–10D, col. DIN Type 710) consists of sintered alumina with a very small amount of SiO_2, the milling time determines the quantity of SiO_2 ground off the inner surface of the mill and so added to the mill-batch.

Therefore the milling time (with Prokorund balls) in a Prokorund mill allows a very fine control of the desired sintering temperature between 1550° and 1650° (Fig. B 12-74).

Figure B 12-75 shows a micrograph of a corundum powder prepared along the foregoing lines and whose density is about 3.85 ± 0.05 g/cm³.

In order to economize on cleaning-acids, the alumina is nowadays often ground, not in Fe mills, but in methanol and with sintered alumina balls in small mills made of pure sintered corundum or in special mills whose lining is rubber held under compression (BLACKBURN, DORST, KRATOCHVÍL). Such rubber-lined mills are made by WILKINSON
[12.6] RUBBER LINATEX LTD., Camberley, Surrey, England, for example. They are well suited to grinding corundum powder down to 15 μ and below; further comminution proceeds so slowly however, that it is best on grounds of efficiency to use the mills described above.

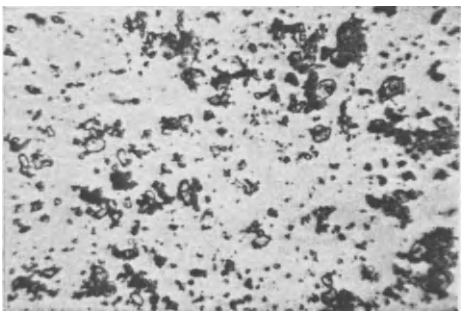


Fig. B 12-75 Micrograph of corundum powder for sintering insulating layers on to cathode filaments (KRATOCHVÍL). Max. grain-size 10 μ

It is simple to convince oneself of the satisfactory purity of an alumina powder by introducing it into very pure methanol tested for resistivity with a probe (Fig. B 12-73, I), shake the suspension for a long time and then allow the powder to settle again. There should then be no appreciable change in the supernatants' resistivity. In spite of its purity, the alumina powder should exhibit cataphoretic properties without addition of ionizing agents like aluminium nitrate. This can also be tested quantitatively by a probe (Fig. B 12-73, II), and determined by the weight of alumina deposited on the tube electrode 8 under fixed conditions of time, voltage, and current flow.

Table T 12–30A contains in No. 1 the chemical analysis of a rather coarse-grained corundum powder such as is commercially obtainable for grinding; in No. 2 is the corresponding analysis of a fine powder (less than 5 μ grain-size) prepared by the methods of Table T 12–30 from the first product, and which was successfully used in continuous production of cataphoretically-deposited insulating layers on cathode filaments. Fine alumina powder of higher purity can be made from synthetic sapphire instead of starting from electro-corundum; this is shown by Nos. 3 and 4 of the table.

The insulation properties of sintered alumina powder can be improved by adding small amounts of BeO (1–2%) to pre-milled and purified powdered alumina (AEG, see also Fig. B 12-75A). This is followed by grinding the mixture in a rubber-lined mill with balls of sintered pure alumina. Example: 2400 g powdered corundum of max.

TABLE T 12-30A. CHEMICAL ANALYSES OF ALUMINA POWDERS FOR MAKING CATAPHORETIC DEPOSITS OF INSULATING LAYERS ON W FILAMENTS FOR I.H. OXIDE CATHODES (KRATOCHVÍL)

NO.	TYPE	IMPURITIES (w/o) SiO_2	Na_2O	Fe_2O_3
1	Starting powder corundum Elektrit 150[1] sieved through 150 mesh/cm²	0.5[2]	0.180	0.038
2	Fine-grain alumina powder prepared from Elektrit by methods in Table T 12-30; $< 5\,\mu$ dia.	0.155	0.135	0.045
3	Synthetic sapphire starting powder[3]	0.034–0.040	0.004–0.011	0.011–0.020
4	Fine-grain ($< 5\,\mu$ dia.) alumina made from synthetic sapphire	0.098	0.013	0.022

[12.6]

(1) Commercial grinding powder (abrasive) made from α-corundum with max. grain-size about 200 μ; Supplier: SPOJ. ZÁVODY NA VÝROBU KARBORUNDA A ELEKTRITU, n.p. (United Carborundum and Elektrit Manufacturers), BENÁTKY N. JIZ. Czechoslovakia.

(2) Including the SiO_2 entrained during pulverization in an agate mortar, since the relatively coarse-grained Elektrit must be comminuted before analysis.

(3) Supplier: SPOLEK PRO CHEM. A HUTNÍ VÝROBU (Association for Chemical and Metallurgical Production), ÚSTNÍ N. LAB., Czechoslovakia.

grain-size 5 μ plus 48 g BeO, the latter made by heating beryllium nitrate crystals ($Be(NO_3)_2 \cdot 3\,H_2O$) till all water and HNO_3 vapors have come off, and followed by coarse grinding in an agate mortar. The Al_2O_3/BeO mixture is then ground for 18 hr in

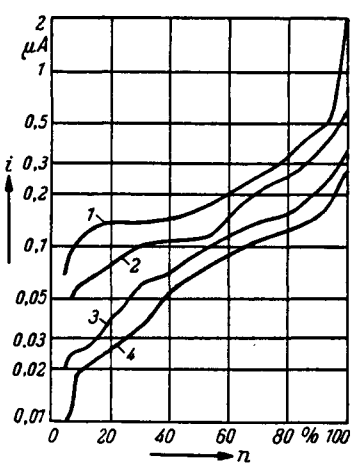


Fig. B 12-75A Distribution curves for leakage current over insulating layers on I.H. cathode filaments; the coatings are made from alumina prepared by different methods and applied as suspensions (BENJAMIN); i = leakage current across insulator; n = percentage of mass-produced tubes with leakage currents less than i

1 Al_2O_3; *2* Al_2O_3 cleaned by liquids; *3* Al_2O_3 pre-sintered at 1750°; *4* Al_2O_3 + 1% BeO

a 10 liter rubber mill. It should be noted, however, that adding BeO increases the sintering temperature (Fig. B 12-76).

In many countries today, alumina powder of high purity, specially for making insulating layers on filaments, can be obtained commercially. Some of the suppliers are:

NORTON Co., Worcester, Mass., USA: "Alundum" acid washed, iron-free; GIGNOUX et Cie, Lyon, France: "Alundum"; DEGUSSA, Frankfurt am Main: aluminium oxide "Vt" or "Ma"; VEB PORZELLANWERKE NEUHAUS: Pastetonerde (alumina paste) "PKU" or "PKU spezial", and "Bitterfelder Pastetonerde reinst". Data provided by DEGUSSA for such material are given in Table T 12–30B.

[12.6]

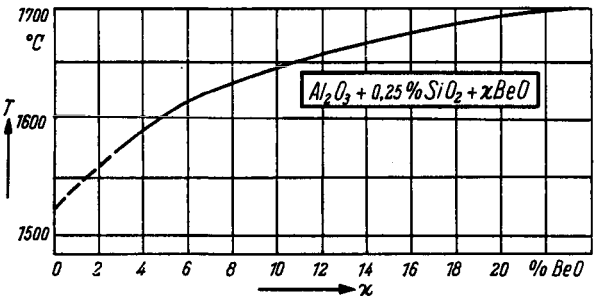


Fig. B 12-76 Temperature T for sintering powder layers of Al_2O_3 + 0.25% SiO_2 on to W filaments, as a function of BeO content (HORÁČEK)

TABLE T 12–30B. PROPERTIES OF SOME COMMERCIAL ALUMINA POWDERS[1] FOR MAKING INSULATING COATINGS ON CATHODE FILAMENTS (MADE BY DEGUSSA, FRANKFURT AM MAIN)

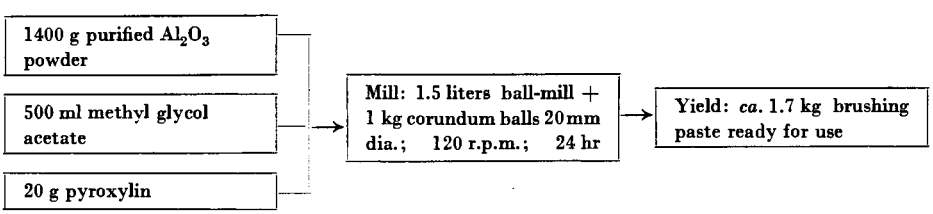
TYPE	STRUCTURE	GRAIN-SIZE	USE
Al_2O_3—Ma	Lamellar	Max. 15 μ 76% less than 6 μ	Spraying
Al_2O_3—Vt	Spheroidal	Max. 15 μ 70% less than 6 μ	Deposition by cataphoresis

[1] Analysis: 99.5–99.7% Al_2O_3, rest typically 0.04% Fe_2O_3, 0.08% SiO_2, 0.25% Na_2O, traces of MgO and CaO.

The high standards demanded of alumina powder (see above) are obviously not required of powder used for brushing insulating coatings on substrates, for example for insulating tube rivets that support mutually insulated components in electron tubes. Table T 12–31 gives instructions for making an alumina paste for brushing.

To prevent discharges across the leads of glow lamps, the leads are often painted with an alumina powder suspension in alcohol.

TABLE T 12–31. INSULATING MATERIAL FOR BRUSHING ON TUBULAR RIVETS


1400 g purified Al_2O_3 powder
500 ml methyl glycol acetate
20 g pyroxylin
Mill: 1.5 liters ball-mill + 1 kg corundum balls 20 mm dia.; 120 r.p.m.; 24 hr
Yield: *ca.* 1.7 kg brushing paste ready for use

12.6.II. *Pure MgO Ceramics*

The starting material is usually fine-grain MgO produced from precipitated magnesium carbonate, briquetted and calcined at 1700° and then ground to about 10 μ sizing in steatite-lined drum mills with steatite balls; this can be done without much entrainment of foreign materials abraded from the mill lining because MgO is relatively soft. Fe mills cannot be used since MgO powder cannot be treated with HCl to remove Fe, being itself strongly attacked by the acid (in contrast to alumina). For molding purposes, the MgO is mixed with a small amount of water plus 2% of a 2% aqueous solution of $MgCl_2 \cdot 6H_2O$; this results in a shrinkage of only 4–5% when fired at 1800–1900°, which avoids crack formation. Experience has shown that MgO compacts readily crack if mixed with too much water. MgO to be extruded is mixed with an organic binder and fired at about 2000° in a highly oxidizing atmosphere (because of the relative ease with which MgO is reduced at high temperature). [12.6]

Since the expansion coefficient of MgO is high (Fig. B 12-64), its thermal shock resistance is poor and crucibles of MgO generally withstand only one heating operation. MgO is resistant to alkalis, but in contrast to Al_2O_3 and BeO is readily reduced in contact with W wire at 1600° (see also MOORE) in accordance with the equation

$$\underbrace{2\,MgO}_{\text{solid}} + \underbrace{W}_{\text{solid}} = \underbrace{2\,Mg}_{\text{vapor}} + \underbrace{WO_2}_{\text{solid}}$$

and the Mg evaporates and condenses on the tube wall; the W burns out by oxidation. For the behavior of MgO with other heater materials see Tables T 12–28 and T 12–31A, for its reactions with other pure oxides in contact with it, see Tables T 12–25 and T 12–31A. In contact with C or graphite it is reduced to metallic Mg in vacuum at 1600°. Although in dry H_2 it is not reduced even at 2500° and its M.P. is 2800°, its maximum usable temperature in the reducing (and generally somewhat moist) atmosphere of the ordinary protective-gas or reduction furnace is only 1600°, because, as stated above, it is easily reduced. In air furnaces with a reliable oxidizing atmosphere, it can be used up to 2400°, however.

The chief use of MgO ceramic in HV technology is for furnace linings in the form of thermal insulation grains, and also as porous, rough-surfaced bodies (water absorption = 10%, see Table T 12–10D, DIN Type 720), for supporting and mutually insulating individual tube electrodes. Dense-sintered MgO crucibles are suitable for vacuum melting of ferrous metals and non-ferrous metals such as Ni, Cr, Cu, Pt, Au, Mn (MICHAELSON).

12.6.III. *Pure ZrO_2 Ceramics*

Pure ZrO_2 has a transformation point (monoclinic to tetragonal) at 1100°, and exhibits so large a volumetric shrinkage that it is hard to process the material by ceramic methods, and it has a very poor resistance to sudden changes in temperature. It can however be stabilized by adding CaO and MgO (often introduced as MgF_2) ([1]CURTIS, [1]DUWEZ, GELLER, [3]WHITTEMORE). Nevertheless, these additives must not be so concentrated that the maximum working temperature of ZrO_2 is appreciably reduced. (For

TABLE T 12-31 A. BEHAVIOR OF SINTERED MAGNESIA CRUCIBLES IN CONTACT WITH OTHER MATERIALS AT HIGH TEMPERATURES ([2]JAEGER: CF. ALSO TABLES T 12-25 AND T 12-28)

REACTION WITH	FURNACE		PHENOMENA
	TEMP. (°C)	ATMOSPHERE	
Be	1600	He	Reaction, penetration
Mo	1400	He	No reaction
	1600	He	No reaction
	1800	He	No reaction
Nb	1400	He	No reaction
	1600	He	No reaction
	1800	He	Weak reaction, formation of Nb_2O_3
Ni	1800	He	Sharply-defined intermediate zone, MgO blackened, melt adheres firmly to crucible
Si	1400	He	Slight change in surface, corrosion, formation of Mg_2SiO_4
	1600	He	
Ti	1400	He	Very slight reaction
	1600	He	Slight reaction and discoloration
	1800	He	Strong attack
Zr	1800	He	Strong reaction
C	1800	Vacuum	Onset of reaction, no adhesion
Mo	1600	Vacuum	Silvery deposit on MgO
W	2000	Vacuum	Reduction of MgO, slight adhesion
BeO	1800	Vacuum	Liquid phase, adhesion of BeO to MgO
ThO_2	2200	Vacuum	Vapor-phase reaction, ThO_2 eroded, no adhesion
ZrO_2	2000	Vacuum	Liquid phase, welding
Al_2O_3	1900	Gas furnace	Spinel formation on alumina surface, no adhesion
$Al_2O_3 \cdot MgO$ (spinel)	1900	Gas furnace	Very weak reaction
BeO	1900	Gas furnace	Powerful reaction, liquefaction
ThO_2	1900	Gas furnace	Very weak reaction
ZrO_2	1900	Gas furnace	Very weak reaction

[12.6]

properties of commercial stabilized ZrO_2, see Table T 12–11 D, DIN Type 730). Stabilized ZrO_2 shows no change in its now cubic structure, even up to high temperatures, and therefore no sudden inflection in expansion characteristic. However α is relatively large (Fig. B 12-77, curve 1: α (20–1450°) = 116×10^{-7}/°C) and so the thermal shock resistance is poor. For this reason, complete stabilization is often waived, and only so much foreign oxide is added as will allow cubic crystals to predominate but enough monoclinic crystals to be left to reduce the overall α appreciably (see Fig. B 12-77, curve 2: α (20–1450°) = 77×10^{-7}/°C); the thermal shock resistance is now correspondingly increased, but irreversibility of expansion in temperature cycling must still remain within tolerable limits. Such zirconia ceramics contain about 4.5–5% CaO and also impurities from the mineral raw materials; as a rule, 0.5–1% SiO_2, 0.4–1% TiO_2, 0.2–0.5% Fe_2O_3 and about 1.5% HfO_2; the M.P. is about 2600° ([3]WHITTEMORE).

Little has so far been published on the question of making dense ZrO_2 ceramics. THOMPSON describes manufacture of crucibles with $ZrCl_4$ addition; the following steps are typical in making very porous zirconia insulator material (21–68% porosity, density 4.4–1.8 g/cm³): the raw materials plus CaO addition are purified by pre-melting in an electric arc, the fusion product is comminuted, molded with an organic binder and fired at 1750° (see [3]WHITTEMORE for details).

Zirconia ceramic is generally used in cases where the operating temperature is too high for alumina (e.g. melting pure Ir at 2440°). Stabilized zirconia up to temperatures of about 1500° has a high enough resistance to be used in ordinary tube construction [12.6] with direct-wound filament wires (Fig. B 12-70). Above 1500° the ϱ value falls so much (Fig. B 12-67) that the oxide itself can be used as a heater (conductor) (DAVENPORT, KEITH, [3]WHITTEMORE).

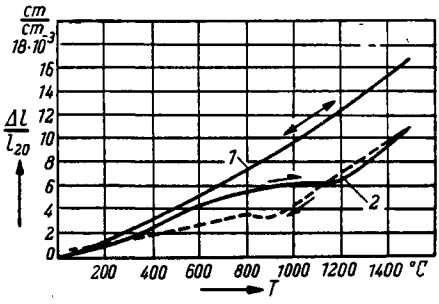


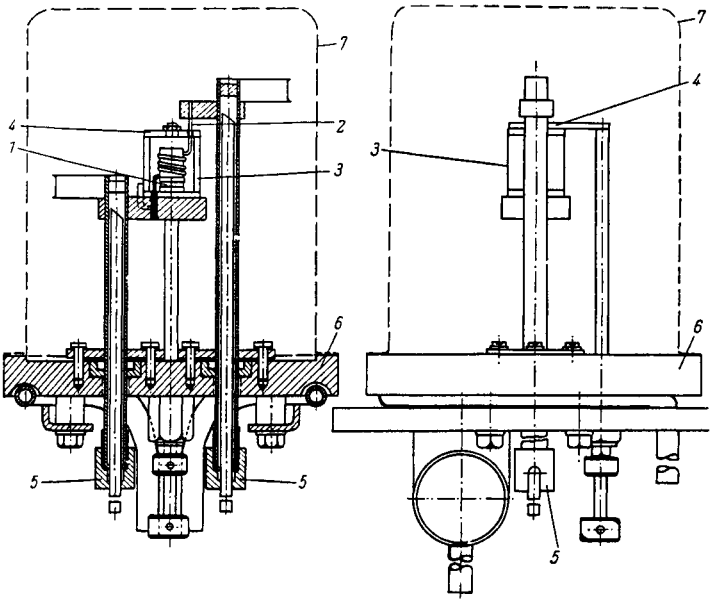
Fig. B 12-77 Expansion characteristics of ZrO_2 ceramics ([2]WHITTEMORE)

1 a fully-stabilized ceramic, wholly composed of cubic crystals, with high α and low thermal shock resistance; *2* a deliberately incompletely-stabilized ceramic, predominantly cubic crystals but with some monoclinic crystals, with reduced overall thermal expansion and correspondingly higher thermal shock resistance

Insulating bricks (Fig. B 12-69A) made of ZrO_2 are mainly used as thermal insulation in high-temperature furnaces up to 2000°, because of the poor thermal conductivity of the material; freely radiating heaters are provided inside the insulators. The W or Mo wires drawn through the insulators serve in this case (unlike that of high thermal conductivity alumina) primarily to support the individual bricks, but also offer the possibility of "pre-heating" the whole insulating wall to reduce the thermal loss. In this construction the walls are divided into separate elements which can easily move relative to each other; this prevents undesirable thermal stresses which can often lead to cracking in solid walls acting as high-temperature insulators, as experience has shown.

Zirconia is soluble in HF, resists molten metals and acidic oxides except silicates, but reacts with basic oxides and forms carbide when in contact with C at high temperature (see Table T 12–25). Since ZrO_2 like ThO_2 does not evaporate much in vacuum up to 2300° (JOHNSON), it is used for H.T. vacuum melting furnaces (see, e.g., Figs. B 12-78, B 12-79) and for H.T. protective gas furnaces for melting materials such as Pt, Pd, Rh, Ru, with the advantage that it does not react with W heaters up to 2000° in the presence of forming gas (75% N_2, 25% H_2) (COHN, cf. however, Table T 12–28 due to KIEFFER). Molten Ti reacts strongly with ZrO_2 stabilized with MgO; under certain conditions better results have been obtained with a crucible material of ZrO_2 + 15 atomic % Ti sintered in vacuum and having a water absorption of only 0.1%, density 5.5 g/cm³ and exceptional thermal shock resistance (WEBER).

[12.6]



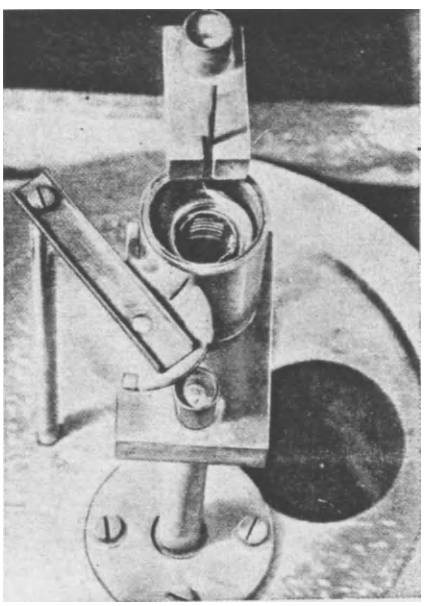


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Fig. B 12-78 Laboratory furnace with resistance heating (max. 1.5 kW approx.); the crucible is high-sintered ThO_2 or ZrO_2 for melting and degassing small charges (a few grams) at temperatures up to 2500°, in vacuums of 10^{-4} to 10^{-5} Torr (ALBERMAN)

1 ceramic crucible; *2* heater coil of W; *3* radiation screens of Ta or Mo, spaced by a coil of Mo wire; *4* sluable metal lid; *5* water-cooled current leads; *6* water-cooled baseplate (brass); *7* vacuum bell-jar made of hard glass; *8* photograph of furnace, taken obliquely from above

A general survey of the behavior of ZrO_2 in contact with metals and oxides is given by Table T 12-31B (see also Tables T 12-25, T 12-28).

Figure B 12-80 shows a special application for Ar-filled spot lamps, used for photocell scanners (picture telegraphy).

ZrO_2 powder often serves as refractory thermal insulation, e.g. for quartz-melting furnaces (see Fig. B 11-3A).

12.6.IV. *Pure BeO Ceramics*

In the preparation of these ceramics, the chief point to remember is that BeO, like other beryllium compounds and the metal itself (see Chapter 5.6), is highly toxic to humans, especially the respiratory organs.

Fig. B 12-79 High-temperature vacuum-melting furnace with tilting crucible of stabilized ZrO_2, resistance-heatedup to 30 kW input, max. temp. 2000°, capacity up to 6 kg steel, ultimate 5×10^{-6} Torr (made by HIGH VACUUM EQUIPMENT CORP., Hingham, Mass., USA)

The following information has been published on the manufacture of dense beryllia: The firm DEGUSSA makes sintered BeO crucibles (see also THOMPSON) up to 130 mm dia., 190 mm high and 7 mm thick, as well as tube up to 600 mm long, 120 mm dia·, by methods described by SLOMAN: pure powder, preferably made by heating the pure

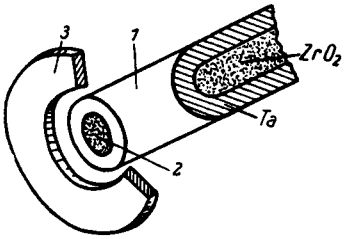


Fig. B 12-80 Gas-discharge spot lamp with Ar filling and ZrO_2 arcing zone (BUCKINGHAM)

1 gas discharge cathode made of Ta tube with ZrO_2 filling; 2 arc point, at high temperature, with some Zr metal in the molten state, produced by reduction in the discharge, and held in place by the porous zirconia substrate; with certain lamps the arc crater is only 75 μ dia.; 3 discharge anode

hydrate or carbonate, is mixed with water; it is then compacted to pieces $17 \times 8 \times 4$ cm³ which are heated in an oxidizing atmosphere to 1000°. (According to [2]RYSCHKEWITSCH preheating to about 1800° is recommended to reduce solution losses during later HCl-leaching to remove Fe.) After cooling, the pieces are crushed to 3–5 mm grit size and dry-milled in Fe mills to 7–20 μ grain-size. Each 100 kg of powder is repeatedly washed

TABLE T 12-31 B. BEHAVIOR OF SINTERED ZIRCONIA CRUCIBLES IN CONTACT WITH OTHER MATERIALS AT HIGH TEMPERATURES ([2]JAEGER; CF. ALSO TABLES T 12-25, T 12-28)

REACTION WITH	FURNACE		PHENOMENA
	TEMP. (°C)	ATMOSPHERE	
Be	1400	He	No reaction
	1600	He	Weak reaction, formation of BeO
Mo	1400	He	No reaction
	1600	He	No reaction
[12.6]	1800	He	No reaction
Nb	1400	He	Weak reaction
	1600	He	Weak reaction
	1800	He	Strong reaction
Ni	1400	He	No reaction
	1600	He	No reaction
	1800	He	No reaction
Si	1400	He	No reaction
	1600	He	Strong reaction, formation of SiO_2
Ti	1400	He	No reaction } Formation of TiO_2, solid solutions of Ti and TiO_2
	1600	He	Weak reaction }
	1800	He	Strong reaction }
Zr	1400	He	No reaction
	1600	He	No reaction
	1800	He	Slight reaction
C	1600	Vacuum	Reduction of ZrO_2, carbide formation at higher temperatures
Mo	2200	Vacuum	Slight adhesion due to sintering, decomposition of ZrO_2 at 2300°
W	1600	Vacuum	Yellow deposit at the boundary region, little change up to 2000°, then marked decomposition of the ZrO_2
BeO	1900	Vacuum	Slight adhesion due to melting, melting complete at 2200°
MgO	2000	Vacuum	Liquid phase, welding at 2000°
ThO_2	2200	Vacuum	Slight adhesion, no liquid phase at 2300°
Al_2O_3	1900	Gas furnace	Strong reaction
$Al_2O_3 \cdot MgO$ (spinel)	1900	Gas furnace	Very slight reaction
BeO	1900	Gas furnace	Slight reaction
MgO	1900	Gas furnace	Very weak reaction
ThO_2	1900	Gas furnace	Very slight reaction

with a total of 300 liters water plus 5% HCl in wooden tubs for 1 hr at 90°, and dried at 110°. The product is now sieved through 1600 mesh/cm^2; molding material is worked up with about 4% traganth and slip-casting material with a small amount of HCl; after drying the green ware, it is fired at 1900° for 7–15 hr in a MgO-lined gas kiln, on zirconia bases.

According to [2]DUWEZ, very dense BeO ceramics can be made in the following way: BeO powder of 1–10 μ grain-size is moistened with a 1% aqueous solution of traganth;

2.5 w/o graphite is added as mold lubricant and the mixture is molded in dies at 3.5 ton/cm². The mold ware is brought slowly to 1500° (100°/hr) in air in a Globar furnace and held at this temperature for 5 hr, during which all the graphite is burnt off and a 1–2% shrinkage takes place. After cooling to room temperature, there is a final burn in an oxyacetylene furnace with MgO muffle for 2.5 hr at 2000°, the BeO being held in ZrO_2 cylinders to protect it from the flames, preferably with a BeO interlayer to avoid contaminating reactions between molding and furnace material (see Table T 12–32).

TABLE T 12–32. ARRANGEMENT OF BeO MOLDINGS FOR FIRING IN MgO MUFFLE FURNACE AT 2000° (CF. ALSO TABLE T 12–25) [12.6]

BeO	} mold ware
	← no contamination of mold ware
BeO	} protective underlayer
	← no liquid-phase formation
ZrO_2	} interlayer
	← no marked reaction
MgO	} furnace muffle material

BeO ceramic has a pure white, rough surface and thin layers are translucent. It has an outstanding thermal shock resistance because of its high thermal conductivity (Fig. B 12-65) and its moderate expansion coefficient. Tensile and compressive strengths of ware so far produced are low compared with other oxide ceramics (cf. Figs. B 12-62 and B 12-63). High-sintered BeO tubes about 300 mm long and 25 mm O.D. with 5 mm wall proved to be vacuum-tight to 1800° ([1]JAEGER), contact with MgO and ZrO_2 being avoided. BeO can be heated in vacuum, He and forming gas without noticeable loss by sublimation up to 2050°, but in the presence of water vapor at temperatures above 1250°, volatile products form which condense to BeO on cooling. BeO is more inert than MgO in the presence of C or CO and can therefore be used in contact with graphite heaters up to 2000°, though in air only up to 1800–1900° according to [2]RYSCHKEWITSCH (cf. Table T 12–25). BeO is rapidly attacked by HF and fused alkalis; it reacts somewhat with cold concentrated HCl, and more rapidly with boiling concentrated HCl; it is only slightly attacked by H_2SO_4 and HNO_3 dissolves it more slowly than HCl. BeO resists attack by alkaline solutions. Table T 12–32A gives a detailed survey of the behavior of BeO in contact with some metals and oxides at high temperatures (cf. also Tables T 12–25 and T 12–28. The high cost of BeO prevents more extensive use of the material (see Table T 12–26).

BeO is used for crucibles to melt Fe, Ni, Pt group metals, Mg or Ca. It is also used to melt pure Be (e.g. as a casting crucible for Be centrifugal castings as per Fig. B 5.6-1, No. 9); it is, however, partly reduced by Ti and Zr.

TABLE T 12-32A. BEHAVIOR OF SINTERED BERYLLIA CRUCIBLES IN CONTACT WITH OTHER MATERIALS AT HIGH TEMPERATURES ([2]JAEGER; CF. ALSO TABLES T 12-25, T 12-28)

REACTION WITH	FURNACE		PHENOMENA
	TEMP. (°C)	ATMOSPHERE	
Be	1600	He	BeO goes black
	1800	He	No penetration, apparently no reaction
Mo	1400	He	No reaction
[12.6]	1600	He	No reaction
	1800	He	No reaction
Nb	1400	He	Slight adhesion
	1800	He	Thin interlayer, corrosion, penetration, blackening of BeO
Ni	1600	He	No reaction
	1800	He	No reaction
Si	1600	He	Slight corrosion of BeO, intergranular penetration
Ti	1400	He	No reaction
	1600	He	No reaction
	1800	He	Corrosion, penetration, blackening of BeO
Zr	1400	He	Slight reaction
	1800	He	Penetration, corrosion
C	2300	Vacuum	Onset of reaction, metal coating on C
Mo	1900	Vacuum	Silvery deposit on BeO
W	2000	Vacuum	Yellow, metallic layer
MgO	1600	Vacuum	Liquid phase, melt adheres to Mo heaters
ThO_2	2100	Vacuum	Melt, fully liquid at 2200°
ZrO_2	1800	Vacuum	Slight adhesion due to melting
Al_2O_3	1900	Gas furnace	Reaction
$Al_2O_3 \cdot MgO$ (spinel)	1900	Gas furnace	Strong reaction
MgO	1900	Gas furnace	Strong reaction, liquefaction
ThO_2	1900	Gas furnace	Strong reaction
ZrO_2	1900	Gas furnace	Weak reaction

12.6.V. *Pure ThO_2 Ceramics*

Since thoria, like other Th compounds and the metal itself, produces radioactive gases, it should be handled with care; in particular, storage vessels with ThO_2 should only be opened in the open air or under an extraction hood.

Manufacture of dense-fired ThO_2 ware from pure ThO_2 by the usual methods is difficult and is only possible by firing at 2000° at least; ThO_2 is first calcined at 1500°, ground in iron mills, the Fe washed out with HCl, and then slip-cast with HCl activation (anticoagulant) or extruded with the addition of organic plasticizers. Because of this difficulty it is common practice to add to the ThO_2 mass 20% $ThCl_4$; or mixtures of low-calcined ThO_2 and $CaCO_3$ are compacted at about 2 ton/cm² and then fired in air kilns for about 1 hr at 1800° ([2]CURTIS). Such ceramics then contain about 0.5–1% CaO.

TABLE T 12–32B. BEHAVIOR OF SINTERED THORIA CRUCIBLES IN CONTACT WITH OTHER MATERIALS AT HIGH TEMPERATURES ([2]JAEGER; CF. ALSO TABLES T 12–25, T 12–28)

REACTION WITH	FURNACE		PHENOMENA
	TEMP. (°C)	ATMOSPHERE	
Be	1600	He	Weak reaction
Mo	1600	He	No reaction
	1800	He	No reaction
Nb	1600	He	No reaction
	1800	He	Weak reaction
Ni	1600	He	No reaction
Si	1600	He	Intense reaction
Ti	1800	He	Reaction; see also Chapter 7.2 (Vol. 1), page 533
Zr	1600	He	No reaction
	1800	He	No reaction
C	2000	Vacuum	Reduction of thoria, carbide formation at higher temperatures
Mo	1900	Vacuum	Slight deposition, adhesion, slight reaction up to 2300°, no adhesion
W	2200	Vacuum	Slight reduction of thoria, slight reaction up to 2300°, adhesion
BeO	2100	Vacuum	Melting, fully liquid at 2200°
MgO	2200	Vacuum	Sublimation, thoria eroded, no adhesion
ZrO_2	2200	Vacuum	Slight adhesion, no liquid phase at 2300°
Al_2O_3	1800	Gas furnace	No reaction
$Al_2O_3 \cdot MgO$ (spinel)	1800	Gas furnace	No reaction
BeO	1800	Gas furnace	Strong reaction
MgO	1800	Gas furnace	No reaction
ZrO_2	1800	Gas furnace	No reaction

[12.6]

See PIERRE on manufacture of ThO_2 ware by casting, using an aqueous slip with polyvinyl alcohol as binder.

Thoria ceramics are the most refractory of all pure oxides (see Table T 12–26) and have the lowest VP (see Fig. B 12-61). No sublimation is noticeable in vacuum up to 2300° (JOHNSON). The thermal conductivity is low and therefore thermal shock resistance is relatively poor. As with ZrO_2, the use of ThO_2 as crucible material is limited to melting metals and acidic oxides (except silicates), since ThO_2 forms compounds with many basic oxides. It is reduced by C above 2000°.

Table T 12–32B gives detailed information on the behavior of thoria in contact with other materials at high temperatures (cf. also Tables T 12–25 and T 12–28).

Because of its high price (Table T 12–26), thoria ware is used mostly for laboratory work, chiefly as crucibles in an oxidizing atmosphere or in vacuum, e.g. for melting Pt metals. Zr, Th and Fe may be melted down in ThO_2 crucibles without wetting the crucible.

12.6.VI. *Spinel Ceramics ($MgO \cdot Al_2O_3$)*

To make these materials, 40 parts by weight calcined MgO and 102 parts by weight calcined alumina are mixed dry, briquetted with a little water and then heated to about 1800°, at which spinel formation goes to completion; after grinding in an Fe mill to about 5–7 μ grain-size and washing out the Fe in dilute boiling HCl, processing is the same as for pure alumina ceramics. The pre-dried green ware is fired at 1900°.

Spinel ware is used for crucibles for special purposes. It is resistant to attack by molten glass and by basic oxides, such as molten PbO, which readily attack alumina. It is [12.7] reduced by C only above 2000°. Spinel ware can be used in vacuum to 1800°.

12.7. Manufacture of Ceramics from Glass

(CORNING, STOOKEY)

Very recently, CORNING Glass Works have marketed a ceramic which they have developed. According to the manufacturer, this material is worked in the glassy state, and then converted by heat-treatment into a more or less crystalline ceramic. The glass

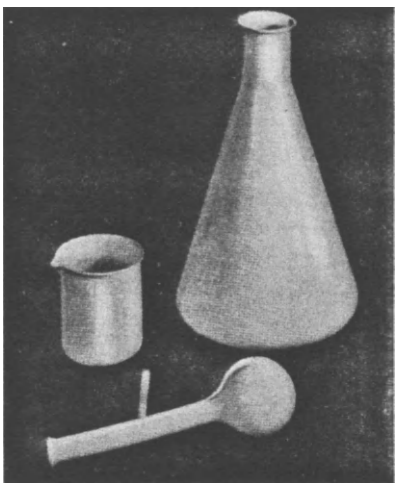


Fig. B 12-81 Vessels made of Pyroceram: they are blown by ordinary glass-working methods and then converted by heat-treatment to predominantly crystalline state (courtesy of CORNING GLASS WORKS)

contains certain nuclei for crystalization, which, after melting, working and cooling of the original glass, produce innumerable, invisibly small crystals when the glassware is reheated. The composition of the original glass and the actual heating process determine the extent and type of crystalization. The resulting material is called "Pyroceram", offered currently in two types—CORNING 9606 and 9608. It is opaque and has almost the same dimensions and shape as the original glass (linear shrinkage on crystalization less than 1%). It is not porous, and therefore is as gas-tight as glass and as homogeneous, having the same expansion coefficient in all directions. It has greater surface hardness

than the original glass and better thermal and electrical properties. Pyroceram 9606 is stated by the makers to permit vacuum-tight joints with metals either after metalization or, with the aid of a solder glass, to seal to metals such as Kovar, W, Mo and (thin-walled?) Cu. [*Translator's note:* ESPE raises the question of the thickness of the Cu

TABLE T 12-33. THE CHIEF PROPERTIES OF TWO TYPES OF PYROCERAM, COMPARED WITH CORNING VYCOR GLASS 7900, CORNING BOROSILICATE GLASS (Pyrex) 7740, AND AN ALUMINA CERAMIC

[12.7]

			CORNING GLASS 9606	CORNING GLASS 9608	CORNING GLASS 7900	CORNING GLASS 7740	Al_2O_3 CERAMIC (93% Al_2O_3)
Density		g/cm³	2.61	2.50	2.18	2.23	3.6
Max. working temp. (1000 hr)		°C	700	–	–	–	–
Softening temperature		°C	1250	1250	1500	820	1700
Specific heat (25 °C)		cal/g °C	0.185	0.190	0.178	0.186	0.181
Mean specific heat (25–400 °C)		cal/g °C	0.230	0.235	0.224	0.233	0.241
Thermal conductivity (25 °C)		10^{-3} cal / cm-sec °C	8.7	4.7	–	2.6	52–58
Thermal expansion coeff. (25–300 °C)		10^{-7}/°C	57	7–20[1]	8	32	73[2]
Tensile strength		kg/mm²	14	11–16	3.5–6.3	4.5–7	18–25
Young's modulus		kg/mm²	12,000	8800	6700	6650	28,000
Knoop hardness (500 g)		–	619	588	477	442	1530
Electrical resistivity	250 °C	Ω-cm	10^{10}	$10^{8.1}$	$10^{9.7}$	$10^{8.1}$	10^{14} [3]
	350 °C	Ω-cm	$10^{8.6}$	$10^{6.8}$	$10^{8.1}$	$10^{6.6}$	$10^{12.95}$ [4]
Dielectric constant	10^6 c/s	25 °C	5.58	6.78	3.8	4.6	8.81
		300 °C	5.60	–	3.9	5.9	–
		500 °C	8.80	–	–	–	9.03
	10^{10} c/s	25 °C	5.45	6.54	3.8	4.5	8.79
		300 °C	5.51	6.65	–	–	–
		500 °C	5.53	6.78	–	–	9.03
Dielectric loss angle tan δ (units of 10^{-4})	10^6 c/s	25 °C	15	30	5	46	3.5
		300 °C	154	–	42	130	–
		500 °C	–	–	–	–	120
	10^{10} c/s	25 °C	3.3	68	9	85	15
		300 °C	7.5	115	–	–	–
		500 °C	15.2	400	–	–	21

(1) Dependent on the heat-treatment in the crystalization process.
(2) Measured between 20° and 500 °C.
(3) Measured at 100 °C.
(4) Measured at 300 °C.

presumably on the grounds that the solder glass can only be joined to Cu by a Housekeeper seal.] Table T 12–33 surveys the properties of the two types of Pyroceram so far available, in comparison with high-silica glass CORNING 7900 and Pyrex CORNING 7740 (borosilicate) and with an ordinary high-alumina ceramic. Figure B 12-81 shows (crystalized) Pyroceram ware.

In the space of this materials handbook, it is clearly impossible to do more than survey the state of development, the properties and the technology of those ceramics which experience has shown come within the province of highvacuum technique and its associated areas. The user of ceramics is recommended always to seek the advice of a ceramicist, *before* starting to develop an electron tube with ceramic components, on the question of the most appropriate type, constructional geometry and conditions of use.

[12.8]

12. 8. References

AEG (ALLGEM. ELEKTRIZITÄTS-GESELLSCHAFT): DRP 610 407/1931/35 (Al_2O_3 + BeO for sintered insulating layers on cathode filaments)

ALBERMAN, K. B.: *J. Sci. Instr.* **27** (1950) 280–282 (Small HV-high-temperature furnace with ceramic crucible and W wire resistance heater)

[1]ALBERS-SCHÖNBERG, E.: *Hochfrequenzkeramik* (Dresden, 1939)

[2]ALBERS-SCHÖNBERG, E. and W. SOYCK in H. STÄGER: *Werkstoffkunde der elektrotechnischen Isolierstoffe*, 2nd ed. (Berlin, 1955)

[3]ALBERS-SCHÖNBERG, E.: *VDE-Fachberichte* **9** (1937) 224–228 (Manufacture, working and properties of Ergan)

AMERICAN LAVA CORP.: Techn. Inform. Chart No. 501: *Mechanical and Electrical Properties of Alsimag Ceramics*, Chattanooga, Tenn. (USA) 1954

[1]ANON.: *Mat. and Methods* (Dec. 1948) p. 80 (Commercially obtainable alumina powder, magnesia powder and stabilized zirconia powder)

[2]ANON.: *Ceram. Ind.* **68** (March 1957) pp. 86–87 (All-ceramic tubes made by Eimac)

[3]ANON.: *Ceram. Ind.* **70** (Jan. 1958) pp. 72–73 (Properties of high-alumina ceramics)

[4]ANON.: *Ceram. Ind.* **69** (Aug. 1957) pp. 89 and 100 (Ultrasonic drilling of alumina support disks for electron tubes)

ANTON, N.: *Ceramic Age* **63** (June 1954) 15–16, 18–19 (Ceramic-body Geiger counters with mica windows)

ASTM: Test standards for ceramics:

C 24 softening temperature;
D 116 electrotechnical porcelain (mechanical strength, breakdown strength, thermal shock resistance, porosity);
D 140 electrical breakdown strength at 60 c/s;
D 150 $\tan\delta$ and ε;
D 256 impact strength;
D 257 insulation resistance;
D 495 arc strength;
D 667 steatite

BAIER, O.: *Fortschr. d. Hochfrequenztechn.* **1** (1941) 422–431 (Electron tubes of ceramic)

BARTH-VUILLEUMIER, G.: *Microtecnic* **3** (1949) no. 2, pp. 68–71 (Production of synthetic sapphire)

BAUKLOH, W. and A. HOFFMANN: *Ber. dtsch. keram. Ges.* **15** (1934) 424 (H_2 permeability of ceramics and silica)

BECKER, E. J. in ASTM Techn. Pub. No. 246: *Cleaning of Electronic Device Components and Materials* (Philadelphia, 1959) (p. 79: permeability of ceramics to H_2)

BENJAMIN, M. *et al.*: *J. Inst. Elect. Eng.* **80** (1937) 401–439 (BeO addition to alumina suspensions for insulation of W filaments in I.H. cathodes)

B.I.R.E. (Techn. Committee): *J. Brit. Inst. Rad. Eng.* **15** (1955) 506–517 (Ceramics for H.F. and electron tube purposes; table of British manufacturers)

BLACKBURN, A. R. and T. S. SHEVLIN: *J. Amer. Ceram. Soc.* **34** (1951) 327–331 (Grinding alumina in methanol in rubber-clad ball-mills)

BONDLEY, R. J.: *Ceramic Age* **58** (July 1951) 15–18 (Properties of American types of ceramic for vacuum purposes)

BOSCH, M.: *Elektrische Bahnen* **11** (1935) 243 (Grid-controlled Hg tank rectifiers)

BOWEN, N. L. and I. W. GREIG: *J. Amer. Ceram. Soc.* **7** (1924) 238–255 (The Al_2O_3—SiO_2 system)
BREWER, L. and A. W. SEARCY: *J. Amer. Ceram. Soc.* **73** (1951) 5308–5314 (SVP of alumina)
BSI (Brit. Stand. Inst.): BS 914–1940 *Test for Laboratory Porcelain*; also BS 1540/1949 and BS 1598/1949
BUBLITZ, G.: *Arch. f. techn. Messen Z.* 974–972 (1938) (Superficial resistance of porcelain)
BUCKINGHAM, W. D. and C. R. DEIBERT: *J. Opt. Soc. Amer.* **36** (1946) 245 (Spot-light gas discharge lamp with zirconia arc-striking point)
BUDNIKOW, P. P.: Technologie der keramischen Erzeugnisse, Berlin 1950
BURNSIDE, D. G.: *RCA Rev.* **15** (March 1954) pp. 46–61 (Vacuum-tight solderable ceramics)
COHN, W. M.: *Z. Techn. Phys.* **9** (1928) 110–115 (Zirconia tube furnaces for use up to 2000°, with W heater windings running in protective gas atmosphere)
CORNING GLASS WORKS: *Pyroceram*; firm's brochure (Corning, N.Y. 1957) **[12.8]**
ČSN ESČ: *Československ. normy 124–1951*: *Keramické hmoty pro elektrotechniku* (Properties and testing of ceramics)
[1]CURTIS, C. E.: *J. Amer. Ceram. Soc.* **30** (1947) 180–196 (Zirconia ceramics with CaO and MgO additions to increase thermal shock resistance)
[2]CURTIS, C. E. and I. R. JOHNSON: *J. Amer. Ceram. Soc.* **40** (1957) 63–68 (Thoria ceramics)
CURTIS, H. L.: *Bull. Bur. Stand.* **11** (1914–1915) 359 (Surface resistance of porcelain)
CUTLER, I. B.: *J. Amer. Ceram. Soc.* **40** (1957) 20–23 (Strength properties of sintered alumina of various porosity grades)
DAVENPORT, W. H. *et al.*: *J. Amer. Ceram. Soc.* **33** (1950) 333–340 (High-temperature electric furnaces using ZrO_2)
DEGUSSA, Degussit Div., Frankfurt a. M.: firm's catalogue (1957–1959)
DEMUTH, W.: *Elektrotechn. Z.* **48** (1927) 1629 (Porcelain, steatite)
DICKINSON, T. A.: *Ceramic Age* **64** (Oct. 1954) 15–17, 33 (Ultrasonic machining of ceramics; Sheffield-Cavitron machine)
DIEPSCHLAG, E. and F. WULFESTING: *Stahl u. Eisen* **49** (1929) 1087 (Resistivity of sintered MgO)
[1]DIETZEL, A. and E. DEEG: *Ber. dtsch. keram. Ges.* **31** (1954) 396–401 (Measurement of anisotropy in opaque poorly-conducting materials such as ceramics)
[2]DIETZEL, A. and N. N. PADUROW: *Ber. dtsch. keram. Ges.* **31** (1954) 7–18 (Composition and transparency of porcelain)
[1]DIN Norm 40 685/I.57; *Keramische Isolierstoffe für die Elektrotechnik.* Group classification and technical properties (Berlin, 1957); recently expanded for the German Democratic Republic by survey pamphlets TGL 211, 1–8, from Dec. 1958
[2]DIN Norm 51 063/12.54: *Bestimmung des Kegelfallpunktes nach Seger* (SK) (Berlin, 1954) (Determination of fall-point of Seger cones)
[3]DIN Norm 40 680/9.54: *Keramische Werkstücke für die Elektrotechnik: Toleranzen* (Berlin, 1954) (Tolerances on electroceramics)
[4]DIN Norm 1064/Juli 1930: *Prüfverfahren für feuerfeste Baustoffe: Erweichen bei hohen Temperaturen unter Belastung* (Testing refractories; softening at high temperature under load)
DOBKE, G.: *Glas- u. Hochvakuumtechnik* **2** (1953) 249–254 (Construction of Hg iron-tank rectifiers)
DORST: Sprechsaal **58** (1925) 838 (Rubber-lined ball-mills)
[1]DUWEZ, P. *et al.*: *J. Amer. Ceram. Soc.* **35** (1952) 107–113 (Stabilized zirconia with CaO addition)
[2]DUWEZ, P. *et al.*: *J. Amer. Ceram. Soc.* **32** (1949) 1–9 (Recrystalization of BeO at 2000°)
EAGLE, J. E.: *Ceram. Bull.* **26** (1947) 272 (Soapstone)
ELLEFSON, B. S.: *Sylvania Technologist* **1** (1948) no. 4, pp. 7–9 (Properties of Alsimag 243 forsterite)
ENDELL, K. and W. STEGER: *Die Erden*; in G. GEHLHOFF: *Lehrbuch der technischen Physik*, vol. 3, pp. 412 to 439 (Leipzig, 1929)
[1]ESPE, W.: *Werkstoffe der Elektrotechnik* (Berlin, 1954); first published in Prague 1950 as: *Hmoty pro elektrotechniku*
[2]ESPE, W., T. LOM and S. VÁGNER: ČSR Patent 85 533/51/55; *Strojnoelektrotechnický časopis* **8** (1957) 80–87; *Vakuumtechnik* **5** (1956) 200–201 (Ceramic electrode centering pieces in lightning arresters)
FAIRCHILD, C. O. and M. F. PETERS: *J. Amer. Ceram. Soc.* **9** (1926) 701–743 (American pyrometric cones and their temperature equivalents)
[1]FRANCL, I. and W. D. KINGERY: *J. Amer. Ceram. Soc.* **37** (1954) 80–84 (Thermal conductivity of oxide ceramics)

[2]FRANCL, I. and W. D. KINGERY: *J. Amer. Ceram. Soc.* **37** (1954) 99–107 (Thermal conductivity of porous alumina)

FRENCHTOWN PORCELAIN CO.: Techn. Bulletin No. 155: *Properties of Frenchtown Ceramics* (Trenton, N.J., USA, 1956)

GALLET, G.: *Le Vide* **12** (1956) 420–423 (Ceramics in electron tube construction)

GANGLER, J. J.: *J. Amer. Ceram. Soc.* **33** (1950) 367–375 (Physical properties of eight refractory oxide ceramics)

GELLER, R. F. and P. YAVORSKY: *J. Res. Nat. Bur. Stds.* **35** (1945) (1) 87–110 (Stabilizing zirconia by addition of MgO and CaO)

GERDIEN, H.: *Z. Techn. Phys.* **13** (1932) 586 (Alumina ceramic "sintered corundum")

[12.8] GOLDAMMER, R.: *Z. Instrumentenkunde* **66** (1958) 72–73 (Detection and localization of inhomogeneities in ceramic bodies by polarized centimeter waves)

GRIESSEL, R. W. in ASTM Techn. Publ. No. 246: *Cleaning of Electronic Device Components and Materials* (Philadelphia, 1959) p. 91, fig. 8: gas yield from an electron tube wall made of forsterite ceramic)

GUND, K.: *Stahl u. Eisen* **23** (1953) 710–713 (Ceramic vacuum-envelope for a 15 MeV electron accelerator); see also SCHITTENHELM

GUNZENHAUSER, A.: *Ceram. Ind.* **37** (Dec. 1941) 41–46 (Production and applications of steatites)

HAGSTRUM, H. D. and H. W. WEINHART: *Rev. Sci. Instr.* **21** (1950) 394 (Porous ceramic for controlled diffusion of gas into vacuum apparatus)

HAUSER, H. H. and A. GUNZENHAUSER: *Ceram. Ind.* **51** (July 1948) 76; (Aug.) p. 74; (Sept.) p. 90 (Steatite)

HECHT, H.: *Lehrbuch der Keramik*, 2nd ed. (Berlin, 1930)

HEIL, A. C.: *Ziegelindustrie* (1952) no. 9/10, p. 362 (Vacuum presses in the fine ceramics industry)

HELDT, K. and G. HAASE: *Z. angew. Physik* **6** (1954) 157–160 (Electrical resistivity of high-vacuum sintered alumina)

HESCHO, Hermsdorf-Schomburg-Isolatoren-Gesellschaft: *Keramische HF-Isolierteile, Fertigung und Gestaltung*, Techn. Informationsschrift Nr. I A-G 809, Hermsdorf (Thüringen, 1942)

HIPPEL, A. R.: *Dielectric Materials and Applications* (New York, 1954)

HORÁČEK, V. from P. HIX: *Vakuová technologie* (Prague, 1954)

HUNT, G. L.: BIOS Final Report No. 30 (London, 1945) (Manufacture of vacuum-tight ceramics wartime developments by Telefunken)

HURSH, R. K.: *J. Amer. Ceram. Soc.* **32** (1949) 75–80 (Betatron tubes of glazed ceramic)

HYDE, N. E.: *Electronic Eng.* **23** (1951) 336–340 (Pyrophyllite, natural ceramic)

HYNES, F. I.: *Ceram. Ind.* **66** (Feb. 1956) 87–91, 102 (Alumina ceramics for vacuum purposes, e.g. magnetron windows)

IJDENS, R. A.: *Philips Techn. Rdsch.* **10** (Jan. 1949) 218–230 (Ceramics and their manufacture)

[1]JAEGER, G.: *Mitteilungsblatt der Deutschen Keramischen Gesellschaft* (June 1949) pp. 51–55 (Be for HV high-temperature furnaces)

[2]JAEGER, G.: *Metall* **9** (1955) 358–366 (Pure oxide ceramics for metallurgical purposes)

[3]JAEGER, G. and R. KRASEMANN: *Werkstoffe u. Korrosion* **3** (1952) 401–415 (Chemical behavior of pure alumina with respect to other materials)

JOBST, G. and F. SOMMER: *Telefunkenröhre* **1** (1934) 8; Brit. Pat. 428 165/33/35 (Screening of insulators)

JOHNSON, P. D.: *J. Amer. Ceram. Soc.* **33** (1950) 168–171 (Behavior of refractory oxides in vacuum at high temperature)

[1]KAŠPAR, J.: *Synthetické korundy* (Prague, 1951) (Synthetic corundum)

[2]KAŠPAR, J., J. ŠMÍD and J. ECKSTEJN: *Monokrystaly* (Prague, 1957) (Single crystals)

KEITH, W. P.: *Ceram. Bull.* **31** (1952) no. 3, pp. 76–8 (Hydrogen furnace with salundum tube and Mo winding)

KIEFFER, R. and F. BENESOVSKY: *Planseeberichte f. Pulvermetallurgie* **5** (1957) 56–71 (Heaters for high-temperatures furnaces)

[1]KINGERY, W. D. *et al.*: *J. Amer. Ceram. Soc.* **37** (1954) 107–110 (Thermal conductivity of pure oxide ceramics)

[2]KINGERY, W. D.: *Ceramic Fabrication Processes* (New York, 1958)

KLÄY, H.: *Bull. schweiz. elektrotechn. Ver.* **44** (1953) 723–725 (Manufacture and properties of porcelain)

KNOOP, F. *et al.*: *J. Res. Nat. Bur. Stds* **23** (1939) (Hardness measuring device)

KOHL, H.: *Ber. dtsch. keram. Ges.* **13** (1932) 70; *Keram. Rdschau* **41** (1933) 75; *Arch. für techn. Messen* (ATM) **1** (1931) 96 (Alumina ceramic "sintered corundum")

KOTTE, I. I.: *Philips Techn. Rdsch.* **16** (July 1954) no. 1, p. 13 (Ceramic bridges for supporting W filaments in projection lamps)

KRATOCHVÍL, V.: *Výroba elektronek a zářivek* (Prague, 1954) (Production of electron tubes and lamps)

LAFORGE, L. H.: *Ceram. Bull.* **35** (1956) no. 3, pp. 117–122, 127 (Power output windows of high-alumina silicate ceramics)

LANG, S. M. and F. P. KNUDSEN: *J. Amer. Ceram. Soc.* **39** (1956) 415–424 (Properties of high-sintered thoria)

LANGER, K.: *Feinmechanik u. Präzision* **51** (1943) 53–58, esp. 57 (Use of ceramic support disks for making electron tubes) **[12.8]**

LEBEDINSKIJ, M. A : *Elektrovakuumnye materialy* (Moscow, 1956) (Materials of electrovacuum work)

LIEBSCHER, I. and F. WILLERT: *Technologie der Keramik* (Berlin, 1955)

LINDSAY, E. W. and L. I. BERBERICH: *Trans. Amer. Inst. Electr. Engrs* **67** (1948) 734–742 (Transition temperatures of ceramic and other inorganic materials used for insulators

LONG, R. E. and H. Z. SCHOFIELD, in REACTOR HANDBOOK-MATERIALS: *General Properties*, chap. 1.3, pp. 41–53 (Beryllia) New York, 1955)

LUKS, D. W.: *Ceram. Ind.* **66** (June 1956) no. 6, pp. 109–112; **67** (July 1956) no. 1, pp. 87–89, 110; **67** (Aug. 1956) no. 2, pp. 97–99 (Alumina ceramics)

LYSAGHT, V. E.: *ASTM Bull.* **138** (1946) 39 (Measurements of Knoop hardness)

MANDERS, TH. J. J. A.: *Philips Techn. Rdsch.* **8** (1946) 72–81 (Ceramic supporting bridges for W filament systems in film projector lamps)

MCQUARRIE, M. J.: *J. Amer. Ceram. Soc.* **37** (1954) (2) 91–96 (Thermal conductivity of oxide ceramics)

MICHAELSON, H. B.: *Mat. and Methods* **38** (Dec. 1953) 110–115 (Properties of refractory oxide ceramics)

MOLTHAN, W.: *Z. Techn. Phys.* **14** (1933) 546 (Interference effects due to stray electrons)

MONTGAILLARD, J.: *L'Onde électrique* **39** (1959) no. 383, pp. 103–108 (On the manufacture of electron tubes with ceramic envelopes)

MOORE, G. E.: *J. Chem. Phys.* **9** (1941) 427–431 (Reduction of MgO by incandescent W)

MORRISON, J.: *Rev. Sci. Instr.* **24** (1953) 230–231 (Gas inlet valve of porous ceramic, flow controlled by Hg)

[1]NAVIAS, L.: *J. Amer. Ceram. Soc.* **15** (1932) 234 (Preparation of small MgO and Al_2O_3 tubes)

[2]NAVIAS, L.: *J. Amer. Ceram. Soc.* **37** (1954) 329–350 (Vacuum-tight ceramics)

[3]NAVIAS, L.: *Amer. Ceram. Soc. Bull.* **38** (1959) 256–259 (Reaction of vapor-phase alumina with Ta at 1900° in vacuum, but not with W)

NEUBAUER, F.: *Sprechsaal* **75** (1942) 297, 417, 451, 473 (Glazes for hard porcelains)

NOLTE, H. J. and R. F. SPURCK: *Television Eng.* **1** (1950) (11), pp. 14–18, 39 (Metalization of zircon ceramics with MnMo)

NORTON, F. H.: *Refractories* (New York, 1949)

NORTON, F. J.: *J. Appl. Phys.* **28** (1957) 36–37 (Degassing of ceramics containing Fe_2O_3)

ORTON CERAMIC FOUNDATION: *The Properties and Uses of Pyrometric Cones*, 3rd ed. (Columbus, Ohio, USA, 1951)

PALATZKY, A.: *Technische Keramik: Herstellung elektro- u. oxydkeramischer Werkstoffe* (Berlin, 1954)

PALMER, R. N.: *Electronics* (Aug. 1954) pp. 162–165 (All-ceramic tubes, assembled on the prefabrication principle)

PECHMAN, A.: *Chem. Engng* **60** (Nov. 1953) 186–190 (Ceramics for high temperatures)

PFESTORF, G. and E. F. RICHTER: *Phys. Z.* **39** (1938) 141–150 (Measurement of the electrical resistance of ceramics at high temperatures)

PIERRE, P. D. S. St: *Ceram. Bull.* **34** (1955) 231–232 (Thoria ceramics made by casting)

PORZELLANWERK NEUHAUS-Schierschnitz, Bezirk Suhl, DDR: Techn. Informationsschrift S 179: Keramische Isolierteile für die HF-Technik (Neuhaus, 1957)

PREIST, D. H. and R. TALCOTT: *Amer. Ceram. Soc. Bull.* **38** (1959) 99–105 Thermal stresses in ceramic cylinders in use as envelopes for vacuum tubes)

PRYSLACK, N. E.: *Ceram. Age* (March 1955) pp. 21–22 (Joints between metals and forsterite)

PULFRICH, H., in M. I. GROSS: FIAT Report No. 560, pp. 3–13 (London, 1945) (Manufacture of Zr-type ceramics for brazed ceramic-metal joints)

RADIO INDUSTRY COUNCIL (England): Proposal RIC/1000 A, Issue 2 (1956)

[1]RIGTERINK, M. D. and R. O. GRISDALE: *J. Amer. Ceram. Soc.* **30** (1947) 78–81 (Porcelains with alkali replaced by alkali earths)

[2]RIGTERINK, M. D.: *J. Amer. Ceram. Soc.* **41** (1948) 501–506 (Microsections of silicate ceramics taken by optical and by electron microscope)

ROBINSON, W. G. and E. C. BLOOR: *Proc. Inst. Elec. Eng.* Pt. II A 100 (1953) no. 3, pp. 247–257 (Electroceramics, their composition and properties)

RÖGENER, H.: *Z. Elektrochem.* **46** (1940) 25–27 (Electrical resistivity of BeO)

ROSENTHAL, E.: *Porcelain and other Ceramic Insulating Materials* (London, 1944)

RUFF, O. and W. GOEBEL: *Z. organ. allgem. Chemie* **133** (1924) 228 (Sintering pure oxides)

[1]RUSSELL, R. and L. I. BERBERICH: *Electronics* **17** (May 1944) 136–142, 338 (Ceramics containing zircon)

[12.8] [2]RUSSELL, R. and W. G. MOHR: *J. Amer. Ceram. Soc.* **30** (1947) 32–35 (Properties of zircon porcelain)

[3]RUSSELL, R.: *The Electrical and Technical Ceramic Industry of Germany*, FIAT Final Report No. 617 (London, 1947)

[1]RYSCHKEWITSCH, E.: *Ber. dtsch. keram. Ges.* **22** (1941) 54–65, 363–371; **23** (1942) 243–260 (Mechanical properties of sintered oxides)

[2]RYSCHKEWITSCH, E.: *Oxydkeramic der Einstoffsysteme* (Berlin, 1948)

[3]RYSHKEWITCH, E.: *J. Amer. Ceram. Soc.* **34** (1951) 322–326 (Torsion modulus of pure oxide ceramics)

SABOL, F. P.: *Ohio State University Research Foundation Project* **252** (1947) (Properties of refractory oxides)

SALMANG, H.: *Die Keramik: Phys. u. chem. Grundlagen*, 3rd ed. (Berlin-Göttingen-Heidelberg, 1954)

SCHÄTZER, L.: *Keramik (Roh- und Werkstoffe, Prüfmethoden)* (Berlin, 1954)

SCHAUDINN, K.: *VDE-Fachberichte* **10** (1938) 139–143 (Electrolytic conduction in porcelain at high temperatures)

SCHITTENHELM, R.: *ATM* (Oct. 1955) p. 226 (Ceramic vacuum envelope for a 15 MeV electron accelerator); see also GUND

SINGER, M.: *Sprechsaal* **84** (1951) 394 (Porcelain base-glass)

SLOMAN, H. A.: *The Beryllium Industries of Germany and Italy* (1939–1945), FIAT Report No. 522 (London, 1946) pp. 29–31: Refractories (Manufacture of rod and tube from BeO)

[1]SMOKE, E. J.: *Ceram. Age* **63** (June 1954) 20–21, 38 (Thermal shock resistance)

[2]SMOKE, E. J.: *J. Amer. Ceram. Soc.* **34** (1951) no. 3, pp. 87–90 (Ceramics with negative thermal expansion coefficient)

[3]SMOKE, E. J.: *Ceram. Age* **61** (1953) no. 2, p. 15 (Zircon ceramics)

[1]SNYDER, C. L.: FIAT Final Report No. 278, pp. 28–31 (London, 1946) (Steatite-magnesia manufacture)

[2]SNYDER, C. L.: FIAT Final Report No. 278, pp. 9–17 (London, 1946) (Manufacture of very pure alumina and alumina-type ceramics at BOSCH, Stuttgart)

SOMMERFELD, A.: *Plastische Massen* (Berlin, 1934) (Rubber, ceramics, glass, asbestos)

SOYCK, W.: *Elektrotechn. Z. (ETZ)*, B 7 (1955) 362–365 (Ceramics in electrotechnology)

STANISLAW, S.: *Ceram. Age* **64** (July 1954) 15–19, 57 (Dry-molded precision ceramics for electron tube manufacture)

STEATIT-MAGNESIA, A. G., Lauf/Pegnitz: private communication 1957 (Properties of recent ceramics, not yet standardized)

STEYSKAL, H.: *Arbeitsverfahren und Stoffkunde der Hochvakuumtechnik. Technologie der Elektronenröhren* (Mosbach, 1955)

STOLL, H. in C. RINT: *Handbuch für Hochfrequenz- und Elektrotechniker* (Berlin, 1955) (vol. III, p. 421–429: German ceramics); see also *Silikattechnik* **10** (1959) 489–491

STOOKEY, S. D.: *Ceramics from Glass.* Preprint of *Appl. Phys. Lab. of Johns Hopkins University* (Baltimore, 1956)

SULLY, A. H. *et al.: Brit. J. Appl. Phys.* **3** (1952) 97–101 (Radiance of oxide ceramics)

TELEFUNKEN G.m.b.H.: Brit. Pat. 503 076/1936/39 (Manufacture of ceramic electron tubes without pumping stems)

THIESS, L. E.: US Pat. 2 511 679/48/50 (Vacuum-tight zircon-talc ceramics)

THOMPSON, J. G. and M. W. MALLET: *J. Res. Nat. Bur. Stds* **23** (1939) 319–337 (Manufacture of highly refractory crucibles)

[1]THURNAUER, H.: *Mat. and Methods* (Dec. 1947) 87–92 (Survey of the properties of technical ceramics)

[2]THURNAUER, H. in A. R. VON HIPPEL: *Dielectric Materials and Applications* (New York, 1954) pp. 179–189

[3]THURNAUER, H. and A. R. RODRIGUEZ: *J. Amer. Ceram. Soc.* **25** (1942) 443–450 (Composition of steatite)

[4]THURNAUER, H.: *Tele-Tech* **6** (Feb. 1947) 86–87, 130 (Low-loss forsterite Alsimag 243)

UDY, M. C. and F. W. BOULGER: *The Properties of Beryllium Oxide*; Battelle Memorial Inst. BM I-T-18 (Dec. 1949)

ULLMANN, F.: *Enzyklopädie der technischen Chemie*, 2nd ed. (Berlin 1928/40); corundum see vol. 7, pp. 15 to 20 (Synthetic corundum); sapphire see vol. 4, pp. 118–137 (Gemstones)

[1]VATTER, H.: DRP 721 415/35/42; DRP 714 139/38/41 (Inert gas filled lightning arresters with tubular ceramic envelopes)

[2]VATTER, H.: DRP 689 504/1938/1940 (Sintering Fe coatings to steatite to make a vacuum-tight bond and produce a layer that can be brazed)

[1]VDE: Prüfnorm 0335/7.56: *Leitsätze für die Prüfung keramischer Isolierstoffe* (Testing ceramics)

[2]VDE: Prüfnorm 0303/10.55: *Leitsätze für elektrische Prüfungen von Isolierstoffen* **[12.8]**

VÚEK (VÝZKUMNÝ ÚSTAV ELEKTROTECHNICKÉ KERAMIKY, HRADEC KRÁLOVÉ) (Res. Inst. for Electrotechnical Ceramics, Königgrätz): micrographs of various types of ceramic, kindly provided by VÚEK

WARDE, J. M.: *Mat. and Methods* **44** (Aug. 1956) no. 2, p. 131 (Properties of oxide ceramics)

WEBER, B. C. *et al.*: *J. Amer. Ceram. Soc.* **40** (1957) 363–373 (ZrO_2 ceramics with 15 atomic % Ti addition for melting Ti metal)

WEBER, H.: *Die elektrischen Metallfadenglühlampen* (Leipzig, 1914) (Filament lamps)

[1]WHITTEMORE, O. J.: *Mat. and Methods* (Dec. 1948) 79–81; *J. Amer. Ceram. Soc.* **32** (1940) (2), pp. 48–53 (Ceramic oxides)

[2]WHITTEMORE, O. J. and N. N. AULT: *J. Amer. Ceram. Soc.* **39** (1956) (12), 443–444 (Expansion coefficients of pure oxide ceramics in the range 0–1550°)

[3]WHITTEMORE, O. J. and D. W. MARSHALL: *J. Amer. Ceram. Soc.* **35** (1952) 85–89 (Stabilized ZrO_2 ceramics)

WILLIAMS, P. D.: *Phys. Rev.* **78** (1950) 353 (Mass-spectrographic analysis of gas given off from ceramics)

WILLIAMS, R.: *Ceram. Age* **63** (1954) no. 7, pp. 41–52, 55–57 (Manufacture and machining of special ceramic bodies used for vacuum tube construction)

WOLF, I.: *Bull. schweiz. elektrotechn. Ver.* **44** (1953) 717–723 (Properties of commercial technical ceramics of Swiss manufacture)

CHAPTER 13

MICA

[13.1] (²Anon., Chowdhury, Keinath, Liebscher, Mica Fabricators Assoc., Miner, Mohr, Schröder, Zeitler)

13.1. General (Occurrence, Extraction, Composition)

Mica is the collective name for various crystalline, hydrated K-Al-silicates which occur in nature as transparent foliated minerals. Only two sorts are suitable for vacuum work:

(a) Muscovite, mostly light-red translucent K-Al-hydrosilicate $K_2O \cdot 3\,Al_2O_3 \cdot 6\,SiO_2 \cdot 2\,H_2O = (Al_2)\,(AlSi_3)O_{10}(OH)_2K$, known as potash mica because of its composition and also as ruby mica from its color. The name "muscovite" comes from the town of Muskovy in Russia where this mica was originally found. The main source is India, the largest world exporter of mica; the bright to dark pink Calcutta mica and the bright to dark green Madras micas are particularly well known. Other sources are Rhodesia, East Africa, Brazil, Argentine, Siberia and Korea (Verman).

(b) Phlogopite, mostly yellowish, a K-Mg-Al-double silicate

$$(Mg_3)\,(AlSi_3)(O_{10})(OH, F)_2K,$$

known as magnesia mica because of its high MgO content, and amber mica because of its color. The colors of individual phlogopites depend strongly on their chemical compositions; besides the best-known yellowish amber mica, there are red-to-brown types with high F content, while the green types contain little F, and mica containing Li is pink. The chief sources are Madagascar and Canada, and to a lesser extent the Indian province of Travancore.

Mica is generally mined in the form of large blocks ("books"). The book is hand-worked by cutting off the usually damaged and contaminated edges to free it from foreign minerals and ores. It is then split with special knives and sorted by certain standards which differ with the market and with local custom. According to the custom of American importers, the lowest grade is assigned to pieces less than 1 in² (grade number 7) and the highest grade is for sheets over 100 in², OOEE Special (*O*ver *O*ver *E*xtra *E*xtra Special) (see Table T 13–1, I). Within the individual size gradings the mica is classified again by appearance and purity (¹ASTM), and the grades are listed in Table T 13–1, II, with their original names.

For electrotechnical purposes, a similar classification by size and quality has been propounded in Europe (Table T 13–1A); the price depends mainly on the size of the usable area, the purity and the clarity. Otherwise, as far as qualitative classification is

TABLE T 13–1. SIZE GRADES AND QUALITATIVE CLASSIFICATION OF MUSCOVITE ACCORDING TO [1]ASTM D 351–49 T

I. Size grades

SIZE GRADE	MAX. RECTANGULAR AREA THAT CAN BE CUT FROM THE PIECE (in²)	SMALLEST SIDE (in)
OOEE Special	100 and above	4
OEE Special	80–100	4
EE Special	60–80	4
E Special	48–60	4
A-1 (Special)	36–48	4
No. 1	24–36	3
No. 2	15–24	2
No. 3	10–15	2
No. 4	6–10	$1^1/_2$
No. 5	3–6	1
No. $5^1/_2$	$2^1/_4$–3	$^7/_8$
No. 6	1–3	$^3/_4$
No. 7	less than 1	($^3/_4$)

[13.1]

II. Visual qualitative classification(1)

CLASS	COMMERCIAL DESIGNATION
V-1	Clear(2)
V-2	Clear and slightly stained (S.S.)(3)
V-3	Fair stained (F.S.)(4)
V-4	Good stained (G.S.)(5)
V-5	Stained, A quality (6)
V-6	Stained, B quality (6)
V-7	Heavy stained(7)
V-8	Black dotted
V-9	Black spotted
V-10	Black stained

(1) Classes V-1 to V-4 are the chief ones of interest for tube construction.
(2) Specially transparent, without mineral inclusions or included air bubbles; if dropped on a glass disk should emit a tone as clear as a piece of metal dropped on the disk (KRATOCHVÍL).
(3) Slight tinting. (4) Tolerable tinting. (5) Allowable tinting. (6) Discolored.
(7) Strongly discolored.

concerned, views that hold, for example, in Bengal are different from those in Madras or in other countries. Nevertheless, it should be borne in mind that really clear pieces without inclusions and flaws are quite rare; but they should be preferred for vacuum work, especially for insulating bridges in H.F. tubes, on grounds of low surface conductivity, low outgassing in vacuum and low dielectric loss. Mica shot through with air bubbles but otherwise clear is unusable for vacuum purposes.

Table T 13–2 gives a rough survey of the chemical compositions of the two chief types of mica. Variations in values are large because of diversity of sources. The usual impurities are oxides of iron, silica and clay (alumina). Natural mica always contains chemibonded water (of crystalization) which cannot be driven off without damaging the whole

TABLE T 13-1A. SIZE AND QUALITY OF RAW MICA (LIEBSCHER)

SIZE NO.	DIMENSIONS (mm)		QUALITY ACCORDING TO CLARITY	NOTES
	LENGTH	WIDTH		
0000	200–300	150–300	40–80	(1)
000	180–300	120–200	34–53	
00	120–200	100–120	28–43	
0	120–190	80–110	22–36	
[13.1] 1	100–180	70–100	16–22	
2	80–150	70–90	10–18	
3	80–120	60–70	6–14	
4	50–100	40–60	4–10	
5	40–60	30–40	2–6	
6	25–30	20–30	1–3	(2)

(1) Sizes 0–0000 are rare and therefore very expensive.

(2) Since sizes 3–6 are the only ones considered for ordinary electrical machines, size 6 is assigned quality (about) 1.

structure (see below). From the crystallographic viewpoint, mica is a biaxial crystal, but the angle between the axes differs widely from type to type. The optic angle for muscovite is 35–75°, for magnesia mica 0–20°; in the first case the plane of the optic axis is normal to the (010) plane, in the second the two planes are parallel. This permits a simple method for distinguishing between the two types: the field of view of a polariscope is darkened by crossing the polarizer and analyzer, and if the mica under test is inserted and produces a bright field (the field of view changing from dark to bright to dark as the mica sheet is rotated through 90°) then generally the sample is muscovite; if it is phlogopite, there is no (or almost no) brightening since it corresponds in effect to a uniaxial crystal.

TABLE T 13-2. CHEMICAL COMPOSITION (w/o) OF MUSCOVITE AND PHLOGOPITE MICAS(1)

COMPOSITION / CONSTITUENT	MUSCOVITE			PHLOGOPITE		
	(2)	(3)	(4)	(2)	(3)	(4)
SiO_2	45.2	45.7	35–59	39.6	41.2	35–45
Al_2O_3	38.4	37.1	23–43	17.0	16.3	11–20
K_2O	11.8	11.2	11.8	9.9	9.8	5–11
MgO	–	Trace	–	26.3	16.3	10–30
Fe_2O_3	–	0.4	Trace(5)	0.5–9.0	10.7	0.5–23(5)
F	–	0.3	(6)	2.2	1.9	(6)
H_2O	4.6	4.9	2–13	3.0	3.2	3

(1) See also HORTON.

(2) Theoretical composition according to BIELER.

(3) WILLIAMS.

(4) According to Czech Standard ČSN–ESČ 125–1947.

(5) $Fe_2O_3 + FeO$.

(6) Not measured.

13.2. Working Mica

Mica can be worked up by splitting, cutting, punching out, drilling and shaping (milling, etc.).

The most noteworthy feature of mica is the ease of splitting; in ordinary cases this is done with a fine knife down to 2 μ (*ca.* 0.7 mg/cm^2), but in the laboratory this process can be taken further, for example, with a fine needle under water (BENEDICKS) or with the aid of a water drop (STRONG). Optical thickness gauges (see Chapter 10, especially Figs. B 10-119 to B 10-120B) can be used to find the thickness of transparent sheets, even after installation as windows in vacuum tubes. A special construction for this, with a [13.2]

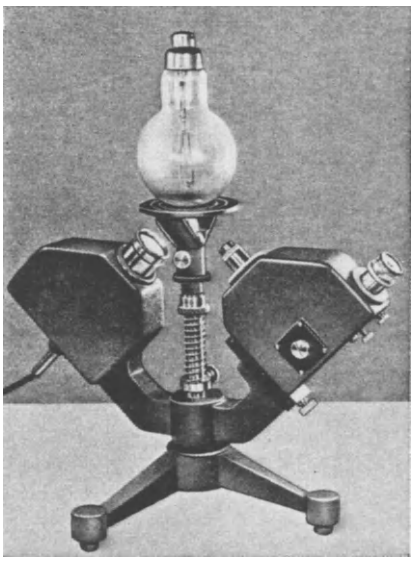


Fig. B 13-1 Optical thickness gauge for thin mica, quartz, glass or transparent plastics; range 1 mm, accuracy 10 μ, can be estimated to 1 μ (made by ROBERT PLAGWITZ, OPT. PRÄZ. ANSTALT, Berlin-Lankwitz, Type GD 12)

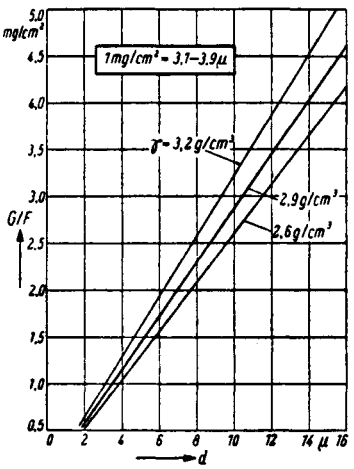


Fig. B 13-2 Relationship between thickness d of mica foil and its mass per unit area G/F for material of density 2.6–3.2 g/cm^3 (mean value 2.9)

micrometer eyepiece, is shown in Fig. B 13-1; it measures very thin sheet mica (and of course quartz, glass and transparent plastics) with a precision of 10 μ, estimated to 1 μ, with a range of 1 mm. The usual procedure with thin mica sheet ($< 30\,\mu$) is not to give the thickness in mm or μ but rather the mass per unit area G/F, in mg/cm^2. [*Translator's note:* this is the usual procedure with *thin* films since it is easier to measure the weight and the area, and divide the ratio of these two by the assumed density than to measure the thickness directly and G/F is a useful parameter for determining stopping power.] Assuming a mica density of 2.6–3.2 g/cm^3, a G/F of 1 mg/cm^2 corresponds to a foil thickness of 3.1 to 3.9 μ. Figure B 13-2 can be used for rapid calculations.

If cutting large pieces by guillotine is not included, the main operation used to work mica is punching out individual disks of desired profile from larger sections. This is shown in Fig. B 13-3. Here, all required holes and notches are made in the same pass. A fine mica dust collects at the edges of the punching which must be continuously extracted from the punch or dust heaps form, and are compressed to a solid, hard layer that can severely damage the tool.

[13.2] In spite of all precautions however, relatively high rates of tool wear are unavoidable. Sufficiently tight tolerances, especially for small electron tubes, can only be held by the use of very massive tools made of a strong steel (e.g. "Poldi Stabil")

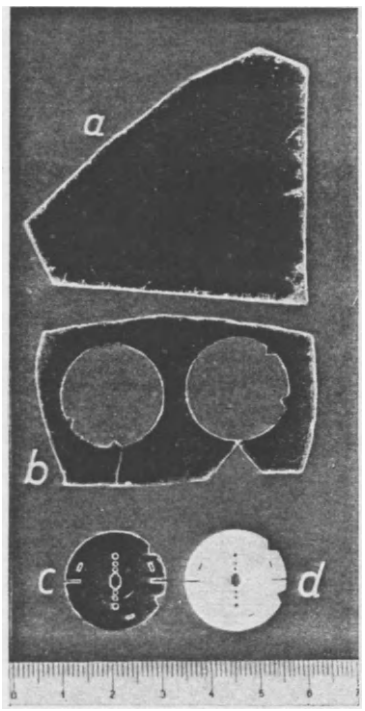


Fig. B 13-3 Punching mica sheet

(*a*) as-supplied mica, before punching; (*b*) the same mica after punching; (*c*) punched mica disk, bare; (*d*) disk after coating with MgO

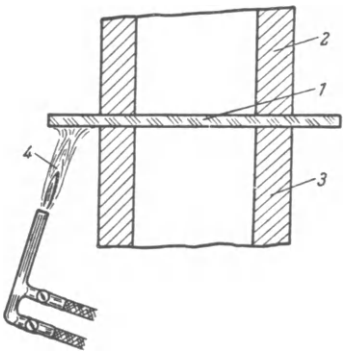


Fig. B 13-3A Removal of the edge of a circular mica window by fire-cutting (to prevent splitting) (MEUNIER)

1 mica disk gripped between two steel tubes whose ends have been ground flat; *2* and *3* steel tubes; *4* oxygas flame for fire-cutting the excess mica

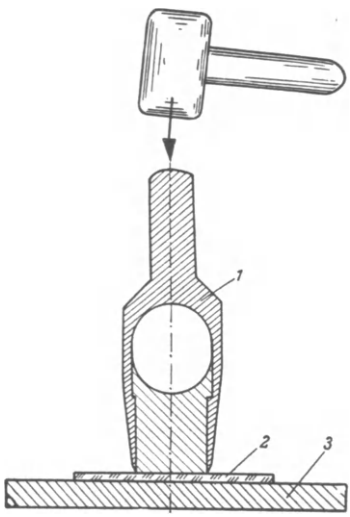


Fig. B 13-3B Punching out thin mica circular disks with a hollow drift

1 steel tool; *2* mica; *3* fairly hard but elastic rubber pad

with very precise guides and excellent fit. The cut edges of punched mica disks must be perpendicular and smooth or the tool should be reground. The edge profile of simple shapes can be formed by clamping a large number of sheets together and milling or shaping the block.

The following is a method specially recommended for making cut-outs of thin mica disks with edges free from splitting, used to make sealed-in windows: the disk to be cut is gripped between the plane-ground ends of two stainless steel tubes of precisely equal I.D. and O.D. (Fig. B 13-3A); the edge of the mica projecting from the guard tubes is then "burnt" (calcined) with an oxygas flame and the residue brushed off. A good method proved in practice for punching out thin circular disks is shown in Fig. B 13-3B where a hollow punch and a solid rubber bed are used.

When punching and drilling holes in mica electrode-support disks, it should be remembered that the smallest permissible hole diameter cannot be less than twice the [13.2]

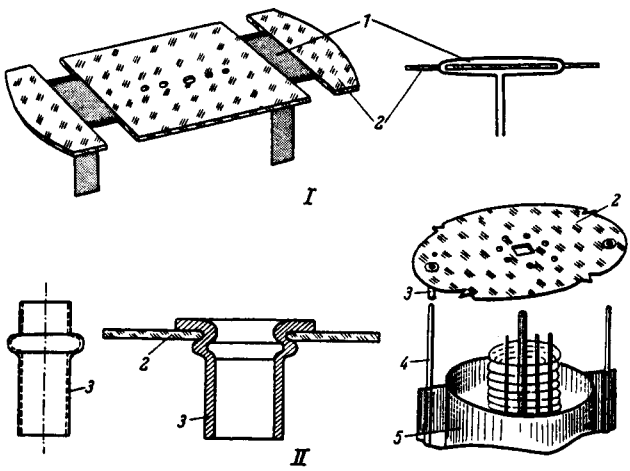


Fig. B 13-4 Mechanical joints between mica and metal
I clamping between straps. II hollow riveting
1 strap; *2* mica plate; *3* hollow rivet; *4* metal support rod; *5* electrode system

sheet thickness. Further, no holes should be made too close to the edge of the sheet because of the danger of a break-out and splitting of the mica; generally, the distance back from the edge (also the separation between holes or other openings) should not be less than 0.5–1.0 mm. When production testing punched or drilled mica sheet for dimensional accuracy with a profile projector (see 9.1, especially Fig. B 9.1-9), the magnification generally recommended is at least $\times 30$, and up to $\times 100$ in the case of very delicate or sensitive electron tubes since here the tolerances on hole-size and gapping are only $\pm 7.5\,\mu$ (WALSH). See [3]ASTM D 652–43 on diameter measurement for fine holes in mica sheet, using a dial gauge to give the depth of penetration of a conical feeler gauge.

The simplest way to make a mechanical joint between mica support disks (of at most 0.2–0.5 mm thickness) and metal piece-parts is to clamp them between small strips or folds attached to the metal components (Fig. B 13-4, I) or to use hollow rivets as per Fig. B 9.3-51*e*, or Fig. B 13-4, II and III.

TABLE T 13-3. PROPERTIES OF TYPES OF MICA ACCEPTABLE FOR VACUUM USE (NOMINAL VALUES)

[13.2]

		MUSCOVITE (RUBY MICA, POTASH MICA)	PHLOGOPITE (AMBER OR MAGNESIA MICA)	REFERENCE
Color		Mostly reddish, also greenish (only slightly tinted)	Mostly fireclay yellow (also green)	
Density	g/cm³	2.6–3.2 (2.8–2.9)	2.6–3.2 (2.65–2.8)	
Onset of calcination	°C	550–650	750–900	
Calcination point	°C	600–800[14] 500–700[15]	900–1100[14] 800–1000[15]	
Temp. for total removal of water	°C	975	925	see ROY and Fig. B 13-5
Melting point	°C	1200–1300	1200–1300	
Temp. for continuous operation in vacuum	°C	*ca.* 350–400		
Mohs' hardness		2.8–3.2 (green muscovite is hardest)	2.5–3.0 (2.78–2.85)	
Tear strength	kg/mm²	∥ [1] 25–30[14]		
Compressive strength	kg/mm²	⊥ [2] 17.7	10.8	
Shear strength (d = 50–500 μ)	kg/mm²	23.5–26.5	10–13	BRITISH ELEC. RES. ASSOC.
Elastic limit (d = 250 μ)	kg/mm²	35–39	20–28	
Young's modulus (d = 250 μ)	kg/mm²	16,000–21,000	15,700–19,400	
Specific heat	$\frac{\text{cal}}{\text{g °C}}$	0.208	0.206	
Thermal expansion coeff.	$\frac{10^{-7}}{\text{°C}}$	∥ [1] 83–98 (20–200°)[13]	∥ 135 (20–200°)[19]	
		⊥ [2] 170–250 (20–300°)[18]	⊥ 162–183 (20–400°)[17] ⊥ sometimes much more[18]	see Fig. B 13-6
Thermal conductivity	$\frac{\text{cal}}{\text{cm-sec °C}}$	$0.6–1.4 \times 10^{-3}$ 1.8×10^{-3} [19]	–	see Fig. B 13-7, see also POWELL
Electrical resistivity	Ω-cm	20 °C: *ca.* $10^{16}–10^{17}$ 500 °C: $10^{8}–10^{10}$	At low temp. less, at high temp. more than for muscovite	see Fig. B 13-8
Surface resistivity	Ω/square	10^{13} [12]	2×10^{12} [12]	see also Fig. B 13-9
$T_{\varkappa 100}$ point	°C	> 500–800		
Te value	°C	> 750 – > $T_{\text{calcin.}}$		
Dielectric constant [10]	ε	$10^{2}–10^{9}$ c/s: 5.4[7] limit ⊥ [2]: 5.7–7.0[19]; 2.5–9[8]	800 c/s: 0.1 mm: Canadian phlogopite: 5–6	see also DANNAT
		India: 2.5–4.7 Canada: 2.9–3.0 S. Amer.: *ca.* 5.9 [16]		
Dielectric loss angle [10]	10^{-4}	60 c/s: (50) 10^{3} c/s: 6 10^{6} c/s: 3 10^{8} c/s: 2 3×10^{9} c/s: 3 [7]	$10^{5}–10^{6}$ c/s: 10 –100[9]	see Fig. B 13-10; $\varepsilon \tan\delta$ at 10^{8} c/s for muscovite up to 300 °C, see Fig. B 12-31 curve 2
		$10^{5}–10^{6}$ c/s: 2 ± 1[13]		
		T (°C) / at 50 c/s 13 / 6 202 / 504 347 / 7360 [5]		

TABLE T 13–3 *(continued)*

		MUSCOVITE		PHLOGOPITE		REFERENCE
Electrical rupture strength	kV/mm	d (mm)	[11]	d (mm)	[11]	see also Figs. B 13-11 and B 13-12[3]
		1.0 0.1 0.01	60–70 200–210 (240–400)	1.0 0.1	50 150	
Voltage for electrical puncture	kV	0.02 mm 0.05 mm	4.0 } [20] 5.0 }	0.02 mm 0.05 mm	3.0 } [20] 4.0 }	
Transparency to thermal radiation		*ca.* 60% that of window glass				
UV transmission threshold	Å	Rhodesian ruby: 2500 Green Congo: 3000 } [4]				POPPER
Gamma-ray transmission	%	Mica thickness: 12 μ; CuK_α rad. 86%				see also Fig. B 13-12A
Beta transmission	%					see Fig. B 13-13
Helium permeability	$\frac{cm^3(NTP)\ mm}{cm^2\text{-}sec\text{-}Torr}$	100 °C : $< 10^{-17}$ 415 °C : $< 10^{-15}$				
Optic angle	degrees	55–75[10] (60–73)[6]		6–20[10] (0–18)[6]		
Refractive index		1.56–1.61		1.58–1.61		

[1] ∥ means parallel to cleavage plane.
[2] ⊥ means normal to cleavage plane.
[3] LINDSAY.
[4] For comparison: synthetic mica $KMg_3(Al \cdot Si_3O_{10})F_2$ with less than 0.05% Fe: 2000 Å.
[6] BOGORODITZKY.
[9] SCHÖLER.
[7] HIPPEL.
[8] Values according to source for sheet mica without air inclusions.
[9] HALL; vary widely according to purity.
[10] Determination is made difficult by possible air, water or impurities between the leaves or sheets; hence fairly divergent results to be found in the literature.
[11] Mostly WILSON's data: measured in air at 20 °C, 50 c/s, and rapid voltage rise; electrode areas = 1 cm².
[12] From SCHRÖDER: measured at 100 V D.C. with the knife-edge contact unit of DIN 53 482, electrode gap 10 mm, knife-edges 100 mm long. The ohmic values so obtained should be multiplied by 10 to get the Ω/square.
[13] EBERT. [14] FISCHER. [15] NITSCHE. [16] WILLIAMS. [17] WOOD. [18] HIDNERT. [19] YARWOOD. [20] LEIZERZON.

13.3. Physical and Chemical Properties of Mica

The chief properties of muscovite and phlogopite mica are collected in Table T 13–3, supplemented by a series of graphs individually referred to in the table. Since mica is a natural mineral that can show very divergent composition and structure according to origin, it will be understood that only approximate and average values can be given, which exhibit large deviations.

The following details concerning mica's properties are emphasized:

Besides its considerable cleavability and flexibility, the most notable property is *relatively high resistance to thermal effects*. Only above 600° does mica alter its characteristics irreversibly in short exposure times. It releases its water of crystalization and becomes calcined, losing its original smooth form. It splits off flakes along the cleavage planes and "inflates"; it loses its transparency, becoming milky, and takes on a silvery white color. Obviously it also loses its good mechanical and electrical properties. The so-defined (short-term) "calcination temperature" differs fairly widely among the

[13.3]

various types of mica. Muscovite is only stable up to 600° because of its higher water of crystalization content, most types of phlogopite are resistant to temperatures over 700°, many types even up to 850°; on the other hand, there are phlogopites that change appreciably even after a short run at 600°; for example $\tan\delta$ will alter. Recent investigations on the weight loss of mica under prolonged heating in air in a Pt crucible show that the release of water of crystalization from muscovite begins as low as 400° (Fig. B 13-5). In agreement with this it is known to be inadvisable to allow large mica components to operate *continuously* in a vacuum tube above 450°. In the case of short-term heating, [13.3] especially for degassing or sintering insulation coatings (see below), higher ratings are obviously possible without appreciable damage. Oxide-cathode receiver tubes may contain mica support disks with closely confined portions, e.g. those in direct contact with the Ni sleeve of the I.H. cathode or with the support wires of highly rated anodes;

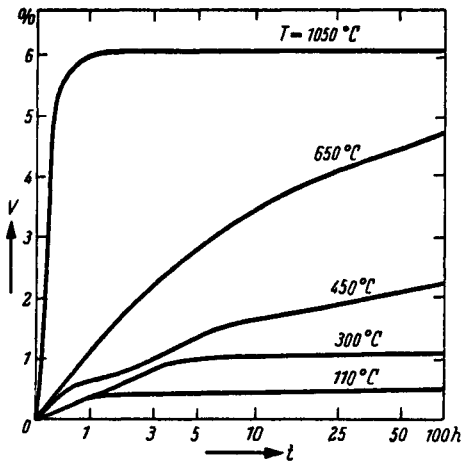


Fig. B 13-5 Weight loss (V) in w/o of powdered muscovite, after heating in air in a Pt crucible at various temperatures T; V is plotted as a function of heating time t (ROY). Onset of calcination is clearly visible, even at 450°, as a continuous but slowly increasing release of water of crystalization; at 1050° calcination is already complete in $1^1/_2$ hr

these portions can reach 600–700°. It is true that they are calcined at the area of contact especially during the forming and pumping processes, but the area concerned is very small because of the very low thermal conductivity of mica, and it seldom breaks away. The gases or vapors released in calcination must be absorbed by an ample getter mirror during the aging process, once the tube has been already sealed off the automatic pumping table.

The *mechanical strength* of mica is relatively high, the values for muscovite being ordinarily greater than for phlogopite. Muscovite is also somewhat harder, more elastic and more flexible than the magnesia types. (A good mica sheet 200 μ thick should be able to be bent over a rod of 50 mm dia. without cracking (see also Fig. B 13-5 A).) Magnesia micas are generally rather brittle and therefore weak at the edges; they can barely be split to sheets less than 10 μ. For all these reasons, muscovite is the preferred material for vacuum technique, especially as entry windows for soft betas in counting tubes.

The Mohs' hardness of mica (scratch hardness) is about 3, and is low compared with glass (4–8). Toothed mica support-disks (Figs. B 13-22, B 13-23) cannot therefore

scratch the glass envelope even when making direct rubbing contact. The low hardness can, however, be a disadvantage in the case of such disks. For example, if tubes fitted with these are brought near motors and thus exposed to vibration, resonance can be set up in the electrode system; the edges of the holes in the mica through which electrode support rods pass are gradually opened up by friction. This results not only in microphonic effects, but the pieces of abraded mica can lead to cathode poisoning.

Thermal expansion figures for the different micas vary very widely according to composition, crystal structure, direction of measurement (normal or parallel to the cleavage planes), impurities and prior heat treatment (EBERT, HIDNERT). It is of [13.3] importance that the α of muscovite between 20° and 400° parallel to the cleavage planes lies in the range of those of soft glasses, and the characteristic on short-term heating to 780° shows no irregularities (cf. Fig. B 13-6). Therefore, reliable vacuum-tight joints can be made between windows of muscovite and soft-glass tubes by cementing (e.g. with Araldite, see Chapter 17) or by sealing via a solder glass (see 13.6).

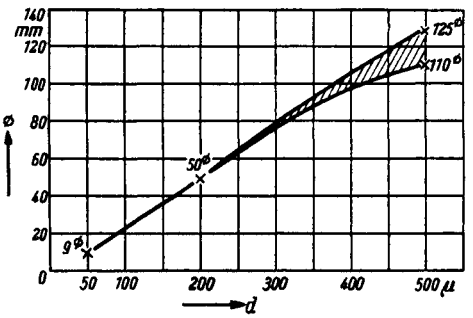


Fig. B 13-5A Diameter of a mandrel over which a good-quality mica of thickness d can be bent without cracking (BRIT. ELEC. RES. ASSOC., and FISCHER)

The *thermal conductivity* of mica ($0.6–1.8 \times 10^{-3}$ cal/cm-sec °C, Fig. B 13-7) is lower than that of those ceramics regarded as poor thermal conductors (2.5×10^{-3}) and lower than that of technical glasses (*ca.* 1.6×10^{-3}). The relatively higher α and low λ mean that very intense thermal shocks can affect the structure of mica; an example would be too-rapid insertion into a hot degassing furnace. This should be specially considered when using mica as supports for photo- or secondary emission mosaic cathodes in TV pickup cameras. For normal purposes, however, the thermal shock resistance is more than adequate.

Electrically, muscovite is better than phlogopite, having higher insulation resistance and breakdown strength. The *resistivity* at room temperature lies between 10^{16} and 10^{17} Ω-cm according to type, provided it is free from conducting inclusions; as in the case of Mg-Al-silicate ceramics, ϱ falls with rising temperature (Fig. B 13-8). The surface resistivity is inferior to that of ceramics since the extremely smooth surface favors formation of conducting layers of condensed impurities. (Directly after splitting, surface resistivity is about 10^{11} Ω/square only, but it rises after a while to the normal value (10^{12} to 10^{13}).) The formation of conducting layers shows up with resistance measurements even in dry air, and below 110° the surface conduction due to adsorbed water layers is clearly detectable (see Fig. B 13-9). See below (13.5) for measures to improve surface resistance and avoid formation of continuous, conducting surface-layers.

Values for *dielectric constant* vary according to the source (see Table T 13–3) and in the case of quality micas rises slightly with temperature (Fig. B 13-9A). Dielectric loss values can also vary considerably according to source. For good, Fe-free muscovite, $\tan\delta$ values may be less than 2×10^{-4} (Fig. B 13-10) but they rise appreciably with temperature (Fig. B 13-10A and BOGORODIZKY). Spotted mica, especially types with Fe inclusions, cannot be used for H.F. tube construction because of high dielectric losses,

[13.3]

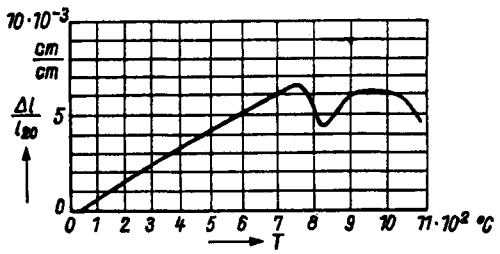


Fig. B 13-6 Thermal expansion coefficient $\Delta l/l_{20}$ of muscovite mica parallel to the cleavage plane (normal to the *c*-axis) as a function of temperature T (ZWETSCH)

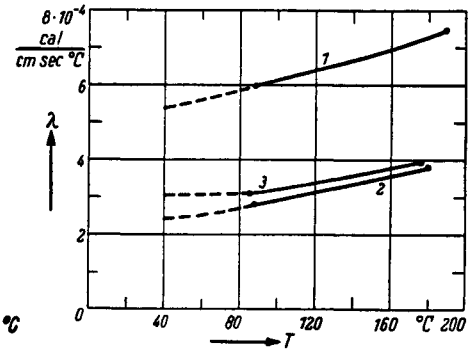


Fig. B 13-7 Thermal conductivity λ of various types of mica for vacuum purposes as functions of temperature T (HAASE)

Curve *1*: India muscovite; curve *2*: Brazilian muscovite; curve *3*: synthetic mica "Terratex"

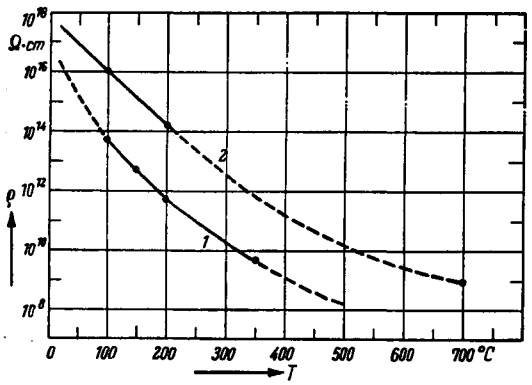


Fig. B 13-8 Electrical resistivity ϱ of muscovite mica as a function of temperature T

Curve *1* from BOGORODIZKY; curve *2*: upper limits reported in the literature for a clean surface and after degassing; measurements made in vacuum

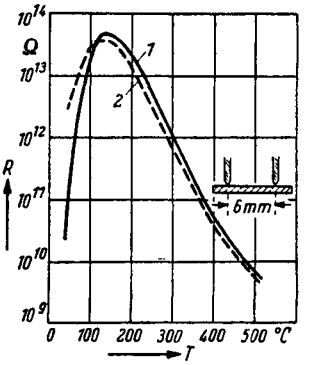


Fig. B 13-9 Electrical resistance R (the sum of surface and volumetric resistance measured in air between two point contacts 6 mm apart); R is plotted for two types of mica used for vacuum purposes, as a function of temperature T at 15% relative humidity (HAASE)

Curve *1*: India muscovite; curve *2*: Brazilian muscovite

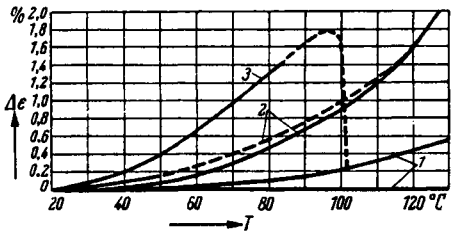
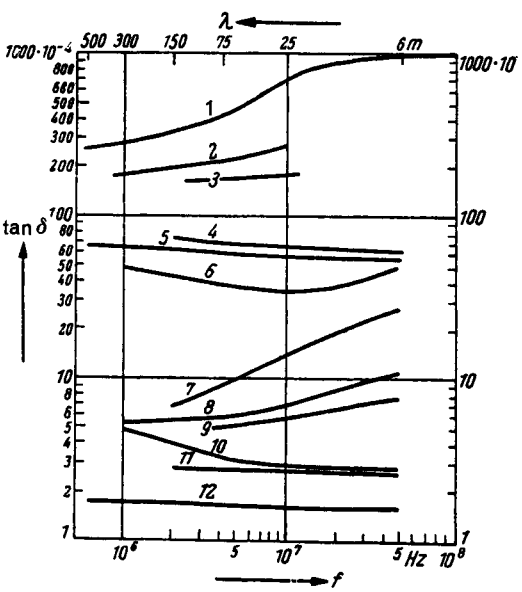


Fig. B 13-9A Capacitance change $\Delta\varepsilon$ of different types of mica as functions of temperature T (DANNAT)

1 red (Calcutta) types; *2* green (Madras) types; *3* yellow (phlogopite) types

[13.3]



CURVE	MATERIAL	DIELECTRIC CONST.
1	Pertinax (for bases)	5.4
2	Bakelite (for bases)	2.8
3	Amberoid (for bases)	2.6
4	Apparatus glass (SCHOTT)	6.5
5	Hard rubber	3.0
6	Thüringer glass	7.1
7	Quartzware	3.8
8	Lead glass	6.7
9	Minos glass (SCHOTT)	7.5
10	Frequenta (Stemag)	6.1
11	Fused silica	4.2
12	Mica (Fe-free)	7.0

Fig. B 13-10 Dielectric loss angle $\tan\delta$ of Fe-free mica at 20° as functions of frequency f and wavelength λ: some other insulating materials are given for comparison (ROHDE, GRUNDKE)

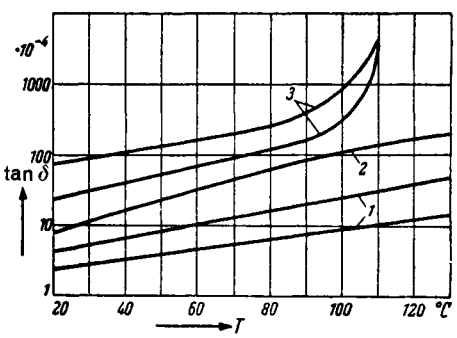


Fig. B 13-10A Dielectric loss angle $\tan\delta$ of various types of mica as functions of temperature T (DANNAT)

1 red (Calcutta) micas; *2* green (Madras) mica; *3* yellow (phlogopite) micas

but can be employed to some extent in L.F. tubes, and for parts of the tube that experience no potential gradients.

The *breakdown strength* of various types of mica depends strongly on the source and rises (relative to 1 mm thickness) as the sheet thickness is less (Fig. B 13-11). Up to about 250–300° this parameter is fairly temperature-independent (Fig. B 13-12).

[13.3]

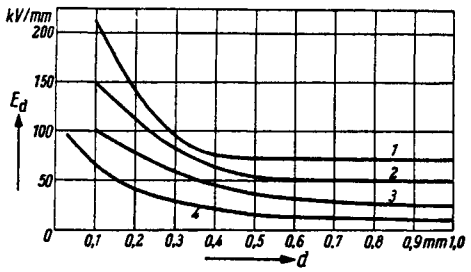


Fig. B 13-11 Electrical rupture strength E_d of various types of mica as functions of sheet thickness d (curves *1–3* from WILSON)

1 muscovite (Bengal ruby); *2* phlogopite (Canadian amber); *3* muscovite (green Madras mica); *4* muscovite, lower limits reported in the literature, measured in air

Optical transparency: a clear mica plate of 25 μ thickness transmits about 90% of normally-incident light. For equal thicknesses, mica windows have a UV transmission not much greater than ordinary glass (Fig. B 10-93). For wavelengths below 2600 Å, mica is opaque (YARWOOD). Likewise its transmission of heat radiation is very low (BURMEISTER), and it will work well as a radiation shield (e.g. to protect glass-metal seals in the foot of a filament lamp (Fig. B 13-28)).

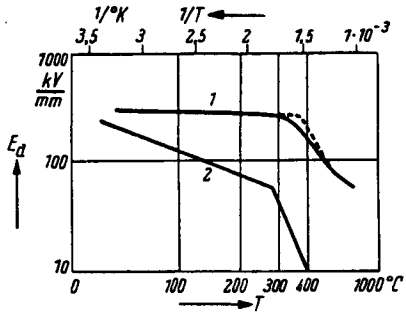


Fig. B 13-12 Electrical breakdown strength E_d of muscovite (*1*) compared with fused silica 0.3 mm thick (*2*) as functions of temperature T (LINDSAY)

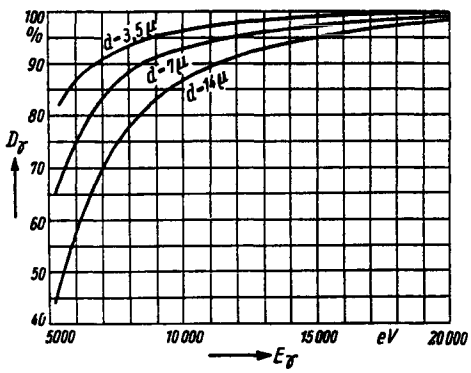


Fig. B 13-12A Transparency D_γ of mica disks of thickness d as functions of the energy E_γ of soft gamma rays (KMENT)

For mica windows in Geiger-Müller counters, knowledge of the transmission for all types of particle and gamma radiation is especially important. Gammas are transmitted without appreciable absorption by the usual mica windows of G/F less than 4 mg/cm², provided the energy is not less than 10–20 keV. Transmission % of very soft gammas through thin mica can be obtained from the group of curves in Fig. B 13-12A. Alpha counting requires extremely thin windows (2–3 μ, i.e. 0.5–1 mg/cm²); however, energetic

alphas are only completely absorbed by mica of G/F 9 mg/cm² (30–35 μ). The transparency of mica to betas of given energy depends almost solely on the G/F value. This is also true for windows of other materials such as Al or thin glass. Figure B 13-13 gives the transparency vs. G/F, but the data only provide rough guide values since the energy spectra of the various beta sources are not fully specified by the maximum energy.

[13.3]

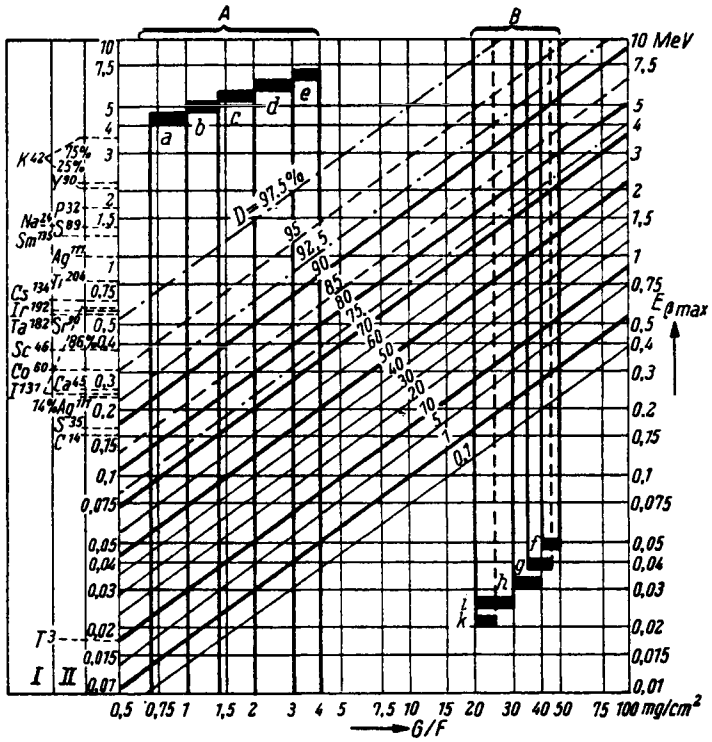


Fig. B 13-13 Transmissivity D of thin foils as a function of mass per unit window area G/F for various maximum energies of beta radiation sources $E_{\beta\,max}$ (BÖHM); nomogram can be used for foils of mica, aluminium, etc., or for thin-walled glass tubing

At the left side of the figure, some important isotopes are given together with their maximum beta energies; col. I includes some $\beta + \gamma$ sources, col. II some sources of βs only. The range of window thickness A comprises the usual "thickness" values for commercial bell counters with mica windows and range B the minimal "thicknesses" attainable in commercial glass-envelope liquid-counters, where a to k denote types of counter made by SIEMENS (cf. also Fig. B 10-100B and associated text)

The *vacuum-tightness* of mica is very high in the direction normal to the cleavage plane. The He permeability at 100° is less than 10^{-17}, at 415° less than 10^{-15} cm³ (NTP) mm/cm²-sec-Torr; this is less than the temperature-dependent He permeability of least permeable glass so far measured (Fig. B 10-82D, curve 1).

The *chemical resistance* of muscovite mica to atmospheric effects is very high. Phlogopite is inferior in this respect. Muscovite is inert to organic vapors (such as quenching gases in counter tubes) and to most acids except HF; phlogopite is, however, sensitive to damage by other acids and is completely decomposed by hot H_2SO_4. The water takeup

of mica sheet is zero normal to the layers; parallel to them, it is generally very low, but if the edges are unprotected water may be absorbed, especially by the softer types. According to LEIZERZON, the water absorption for muscovite is 1.3–4 w/o, and 1.5–5.2 for phlogopite. Mica is completely oil-resistant if the edges of the sheet are well sealed; this is the case with, for example, mica windows joined to a flange with solder glass (see Fig. B 13-19). However, all types of sheet mica with unprotected edges are very sensitive to oil, which penetrates from the edge along the fine clefts parallel to the surface and destroys the mica by exfoliation. This has to be watched when working mica in the
[13.4] machine shop, where experience shows that oil is handled very carelessly, because any damage caused cannot be made good by washing in the solvents normally employed for metals.

13.4. Degassing Mica

This is relatively difficult. On the one hand, the surface layers are saturated with gas, especially adsorbed water vapor, which must be driven off by high-temperature heating before installing the mica piece-part in the electrode system; this is because the gas cannot be released fast enough in the normal pumping schedule of a quick-acting

TABLE T 13–4. DEGASSING MICA COMPONENTS ([1]MO-VALVE)

Ⓐ *Apparatus*

1. Hydrogen stove with resistance-heated quartz tube and water-cooled exit zone as per Fig. B 9.2-15, fed with dry H_2
2. Ni boats, previously degassed for $^1/_2$ hr at 950°.

Ⓑ *Process*

Mica parts loosely packed in Ni boats	→	into stove, 16 min in hottest zone at 675° (+12.5/–25°)	→	16 min in cooling zone	→	Remove, store preferably in evacuated containers

automatic pumping table. On the other hand, so far as possible the water of crystalization (max. 18 w/o) must not (or not appreciably) be extracted in the degassing process, since it is a determining factor in the structure of mica and its properties. No wonder, therefore, that in practice the individual manufacturers often recommend totally different and contradictory methods for degassing and yet have succeeded with them. Careful manufacturers heat only to 200° in air, or better, *in vacuo* but for prolonged periods of up to 3 days (YARWOOD); others recommend 8–15 hr *in vacuo* at 450–500°; yet others recommend degassing at 675°, but only for 16 min (see Table T 13–4). There are, however, firms in which the mica parts are pretreated in a flow of dry H_2 for 1 min to $^1/_2$ hr at 900–950°.

It is important that degassing should be undertaken only after punching out. The degassed parts should not be touched again with bare fingers, should be stored in a dry, dust-free atmosphere, and installed in the vacuum tube in 2–3 days at most, and the tube should then be evacuated at once. If storage time is longer, a vacuum vessel should be used (Fig. B 9.2-19). Mounting should take place as quickly as possible, and in a dry

working space, to cut down readsorption of atmospheric water vapor. Unfortunately, there are types of mica, especially Madagascar ambers, which always prove difficult to use because of intensive outgassing during tube operation, though they do have relatively high clarity (PENOTET). It is therefore recommended that mica disks degassed in the normal way be tested from time to time on a comparative basis; this involves heating in vacuum and inspecting for subsequent outgassing with an ion gauge or mass-spectrometer.

It has been shown that, in oxide-cathode receiver tubes, friction of metal parts (e.g. grid supports) and of the glass wall with mica disks, releases some gas which may noticeably reduce cathode emission; such friction is unavoidable where there are shock [13.5]

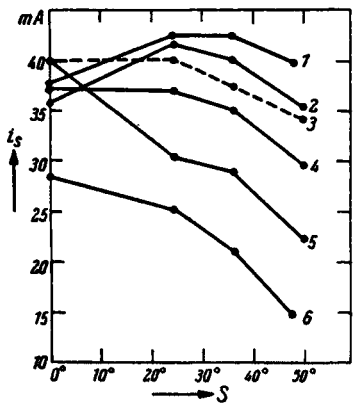


Fig. B 13-14 Reduction of electron emission i_s of an oxide cathode in a receiver tube plotted as functions of intensity $S^{(1)}$ of shock loading; the reduction was caused indirectly by mechanical shock applied to the electrode system supported by mica disks (HOLLAND)

1 clear Brazilian muscovite mica supports; *2* Canadian amber mica; *3* green Madras mica; *4* clear India mica; *5* dark Madagascan amber mica; *6* tube with nine additional mica distance pieces at the head and foot of the electrode system, mica not in contact with cathode

[1] *S* in degrees elevation of the impact pendulum before release, as a relative measure of impact energy

stresses. Individual types of mica can behave very differently in this respect, as shown by Fig. B 13-14.

Water release from mica can be detected when burning off conducting layers with a high voltage discharge, i.e. in the so-called "sparking" of (cold cathode) tubes with a TESLA coil (transformer) or spark coil. In high-voltage tubes, ceramic or silica bridges are therefore preferred for gapping metal components.

13.5. Surface Treatment for Mica

As stated before, the smooth and fault-free surface of mica leads readily to the formation of very troublesome surface layers—particularly noticeable after tube gettering because of stray Ba vapors and condensed metallic vapor from the hot cathode and other electrodes, which always sublime to some extent during intense heating in the

degassing process and even during operation of the tube. The effects of such layers can be lessened by scratching the mica surface over suitable areas with a fine needle (Fig. B 13-15) or by stamping slots to increase the leakage path between electrode supports attached to the mica which require to be carefully insulated from each other.

A simpler and more reliable way is to spray highly insulating oxide layers, which by virtue of their rough surface structure prevent formation of continuous electrical paths

[13.5]

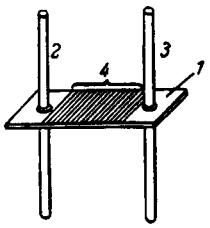


Fig. B 13-15 Increasing the surface insulation of mica by ruling scratch-lines (AEG)

1 mica bridge; *2* and *3* electrode supports; *4* lines scratched on the mica surface between *2* and *3* which are insulated from each other by the mica

along the mica and between electrodes if metallic vapors should condense there. The treatment is the same in principle as that described in 10.4.XII for increasing resistance of glass surfaces (see esp. Fig. B 10-234D). However, for mica, *aqueous* MgO suspensions are preferred; Table T 13–5 contains detailed instructions for making them. There are

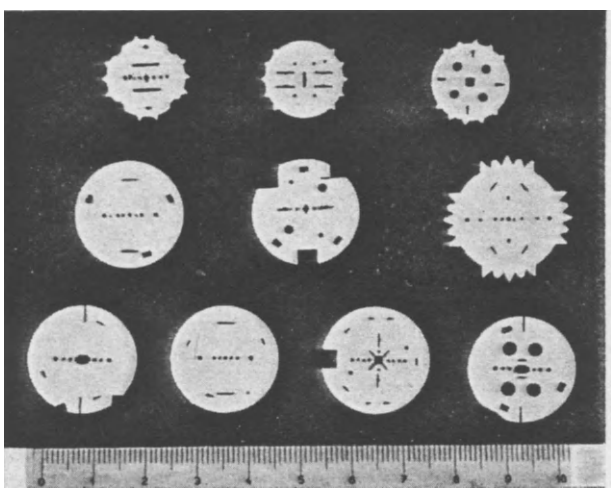


Fig. B 13-16 Stamped-out, degassed mica disks, with sprayed-on MgO insulating layer, as used for ordinary receiver tubes and miniature tubes

other suspensions in use: ZrO_2 or Al_2O_3 based suspensions in methanol, or polyvinyl alcohol, or those with mixtures of MgO, ZrO_2 and Al_2O_3. The mica plates are first well degassed (e.g. 500° for 4–12 hr in an air oven), then laid on a conveyor belt and sprayed from above by continuously operating spray-gun. The mica now passes directly through a tunnel oven and is dried in $^1/_2$ min at 400° so that adhesion of the sprayed layer is sufficient, whereupon the disks are turned over, sprayed and dried on the other side

TABLE T 13–5. SPRAYING SUSPENSIONS FOR IMPROVING SURFACE INSULATION OF MICA DISKS OR PLATES

Ⓐ *Preparation of MgO*

either (A 1): 500 g $MgCO_3$ → Heat 1 hr in electric furnace at 900–1000° in air → Yield: 240 g dry MgO

or (A 2): 250 g MgO, chemically pure DAB6 → Heat for 24 hr in electric furnace at 900° in air → Yield: *ca.* 240 g dehydrated MgO [13.5]

Ⓑ *Preparation of spraying suspension*

(B 1) Simple MgO-water suspension:

240 g MgO made by (A 1) + 1.5 liters distilled water → Ball-mill for 5 min → Filter through fine-mesh bronze screening →

→ Yield: *ca.* 1.6 liters spray paste for *ca.* 4000 mica disks 17–21 mm dia. coated both sides

(B 2) MgO ($Mg(NO_3)_2$)-water suspension:

20 g MgO made by (A 1) or (A 2)
150 g $Mg(NO_3)_2 \cdot 6\,H_2O$, crystalized
500 ml distilled water
→ Grind in 1.5-liter ball-mill with 10 Prokorund balls of 15, 10 of 20 and 10 of 25 mm dia.; 72 r.p.m., for 20 hr. Filter through suction filter with glass filter G 4

Store filtrate (*ca.* 450 ml) for use (1)

Wash filtrate twice, each time with 500 ml hot distilled water, once with 100 ml methanol; dry for 12 hr at 110°, grind, sieve → Yield: *ca.* 24 g dry powder →

→ 60 g dry material
500 ml distilled water
→ Ball-mill in 1.5-liter mill, r.p.m. and ball sizes as before but for 24 hr → Yield: 550 ml MgO spraying suspension. Can be kept for 3 months in glass flasks with ground glass stoppers

(1) The filtered solution, after making up with distilled water to 500 ml, can be added to 20 g MgO to make a new starting material, instead of the one given in the first position of B 2. After every 4 times, 20 g crystalized $Mg(NO_3)_2$ must be added.

in the same way. (In some works, the mica components are sprayed continuously and hot-air dried in a cylinder of wire mesh which rotates, until the necessary insulating layer is obtained.) After spraying, the two layers are sintered at 600° in air for 10 min;

[13.5]

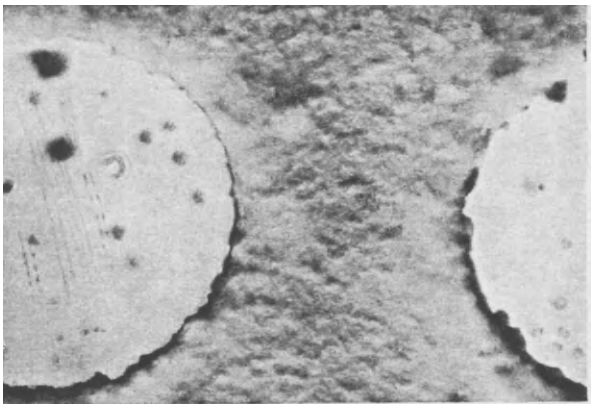


Fig. B 13-17 Photomicrograph (about × 125) of a mica disk coated with MgO insulation (KRATOCHVÍL). The punched holes visible on both right and left of the figure have diameters of 0.75 mm

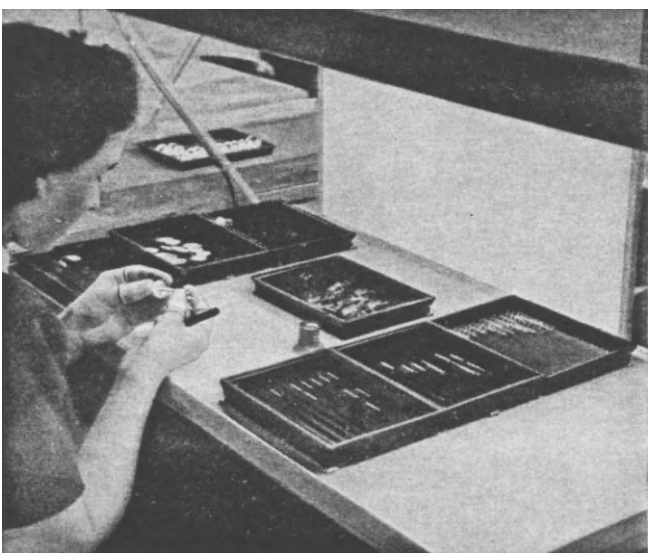


Fig. B 13-18 Assembly of tube electrode system between mica disks; the operation is being carried out by hand with rubber fingerstalls, the mica should only be held by the edges and fine work done with tweezers

many manufacturers sinter for $^1/_2$ hr at 400°. The plates are now coated with a white, rough layer of 50 μ thickness on both sides (Figs. B 13-3, d, and B 13-16). They are stored in sealed containers pumped down at least to rough vacuum (Fig. B 9.2-19);

they should be taken from these containers immediately before assembly. Figure B 13-17 shows an enlarged view taken through a microscope of the surface of one of these plates between two punched holes each 0.75 mm dia.; the figure gives a good illustration of the degree of roughness obtained.

Obviously, mica sprayed with insulating material should not be touched on the flat surfaces but only at the edges and with rubber fingerstalls, as shown in Fig. B 13-18.

One other method of surface treatment that should be mentioned is coating with a thin layer of colloidal graphite; this is applied to many counting-tube windows in order to conduct away wall charges (see, e.g., BROWN). Vacuum-evaporated metal films (see 10.4.V) do not adhere well to mica and can easily be wiped off with a cloth (YARWOOD). [13.6]

Finally, mention should be made of a phenomenon often observed with mica disks in mass-production of radio tubes; the appearance of black deposits associated with poor insulation. This has nothing to do with the mica itself and arises either from incomplete conversion of the alkali earth carbonate coating of the oxide cathode prior to gettering, or is produced by the use of oil-bearing compressed air when blowing off the electrode system after mounting (to remove dust, abraded MgO particles or carbonate particles loosened from the cathode coating in assembly).

The incomplete conversion of cathode coating may arise from faulty heater current connexions on the automatic pumping table; the cathode does not reach forming temperature and carbonate is not turned to oxide. Later when the tube is on the aging rack, decomposition gases from the carbonates (CO, CO_2) are reduced to C by the getter or hot Ni, the C deposits itself on the Ni parts or the nearby mica as a black layer and destroys the insulation properties. This phenomenon is usually coupled with poor vacuum.

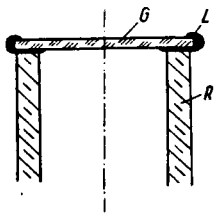
13.6. Sealing Mica to Glass or Metal

It is necessary when installing mica windows of any type to join the mica in a vacuum-tight seal with the actual glass or metal envelope, and if at all feasible to arrange matters so that the whole unit with its window can be degassed on the pump at as high a temperature as possible.

Vacuum-tight joints can be made with Araldite (see 17.3.XII, especially Figs. B 17-12, and B 6.3-7A), but 200° is the highest possible degassing temperature. Small mica windows can be cemented with AgCl to make a vacuum-tight joint (see 17.3.VII), and this will stand up to 300°. Thermoplastic cements have maximum degassing temperatures even less than 200° (see 17.3.XIII) and the same is true of Apiezon wax W (see Fig. B 17-6 and associated text). Powder-glass suspensions have proved better for sealing mica windows to metal or glass flanges; such joints stand up to 400° and have recently come into ever-increasing use (e.g. for commercial counters). The broad outlines have already been given in 10.6.I (Solder glass). The following points are important for good results with such joints:

1. Adequate match of expansion coefficients between mica and partner. The preferred glasses are therefore ordinary technical soft glasses of $\alpha = (85\text{–}100) \times 10^{-7}/°C$, T_{soft} above 600°; for the metal component FeNi (50/50) or ferritic CrFe (*ca.* 25/75) or FeNiCr (52/42/6) or other Fe alloys with similar α (see 6.1).

[13.6]



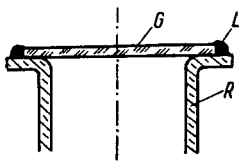
I Author: DONAL (1942)

G: dia. = 50 mm; d = 125–500 μ

R: Corning glass 0080 or 0120 (see Tables T 10-4 and T 10-2, A1) with ground edges for soldering

L: aqueous Pb-borate-silicate brushing paste, α(0–375°) = 98×10^{-7}/°C, T_s *ca.* 450°

P: 5–10 min at 600°, $^1/_2$–1 hr annealing time



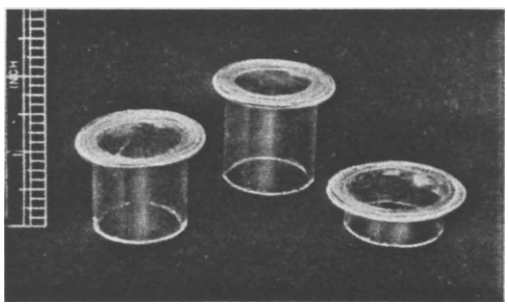
II Author: WU (1947)

G: dia. = 28 mm; d = 5 mg/cm^2 (*ca.* 20 μ)

R: soft glass tube, α *ca.* 90×10^{-7}/°C, with flanged end, sealing faces ground

L: as DONAL above

P: raise to 570° within 1 hr, then cool slowly



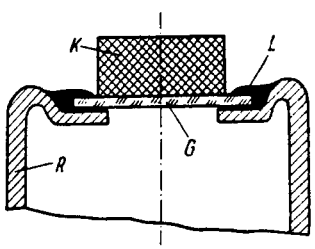
III Author: DALE (1948); cf. also Fig. B 10-264

G: dia. up to *ca.* 40 mm

R: Flanged soft-glass tube of BTH C 19 (see Tables T 10–2 and T 10–4 (E 1)) or copper-plated FeNi (50/50)

L: dry lead-borosilicate glass powder (see Table T 10–34), mica sealing glass BTH C 93 (see Table T 10–2, E1)

P: a few minutes at 500°; cool at 5°/min



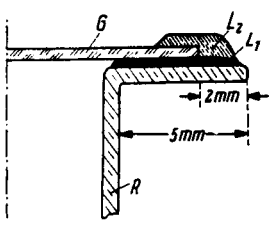
IV Author: MALTER (1946), COLLINS (1948)

G: India mica; dia. = 8 mm; d = 0.13 mm

R: FeNiCr (52/42/6) (see Table T 6.1–6) reduced for $^1/_4$ hr in dry H_2 at 1100° then oxidized in moist H_2 10–15 min at 1100°

L: solder glass CORNING 7570

P: $^1/_4$ hr at 600° in air oven with auxiliary weight *K* made of ceramic (dia. ceramic < dia. mica) to prevent flow of solder glass over disk; color of completed seal should be bright green



V Author: LABEYRIE (1950)

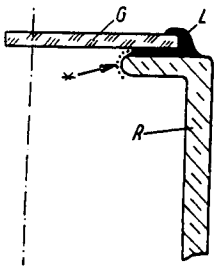
G: *ca.* 30 mm (2–3 mm < flange dia.); d = 10–40 μ

R: glass of α *ca.* 85×10^{-7}/°C; $T_s > 600°$, or FeNi (50/50) or CrFe (30/70) α (85–110) $\times 10^{-7}$

L: aqueous paste of M 130 solder glass (see Table T 10–34) + 5 w/o fine-ground Pyrex (so that $\alpha_{glass} \geqq \alpha_{solder} \geqq \alpha_{mica}$); solder applied in two layers L_1 and L_2 (L_1 about 0.2 mm thick)

P: dry 1 hr; heat in 1 hr to 600°, 15 min at 600°; cool in 3–4 hr from 400° to 20°

Note: seal degassable up to 300° for case of mica 7 μ thick, pressure differential 1 atm



VI Author: MEUNIER (1953)

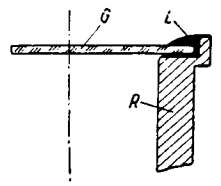
G: as above; d = 1–3 mg/cm², cut as per Fig. B 13-3A

R: ordinary soft glass, α (20–300°) = 95 × 10⁻⁷/°C, inward flange, soldered area ground, inner edge of flange(*) roughened with glass paper and coated with graphite by means of a soft pencil to avoid adhesion of solder glass

L: solder glass M 130 (see Table T 10–34) suspended in xylene or mixture of water + alcohol

P: 3 min at 630–650°, then hood-oven slowly raised in 20 min

Note: This window is stable in contact with liquids which do not attack glass enamels or mica [13.6]



VII Author: ANTON (1954); see also BLEEKSMA and Fig. B 13-32A

G: d = 1–3 mg/cm² (best ruby mica, split to thickness)

R: tube with machined flange, CrFe (25/75)

L: CORNING 7570 (Tables T 10–4, A1, and T 10–34), powder sieved through 100 mesh/in., suspended in distilled water

P: $^1/_2$ hr at 550–600° in oxidizing atmosphere, then annealed at 400° for $^1/_2$ hr

Fig. B 13-19 Sealing mica disk windows to glass or metal tubes with low-melting solder glass; I–III, V–VII, for beam-entry windows of Geiger counters (see Figs. B 13-32, B 13-32A); IV, power-output windows for H.F. energy from USW tubes (see also Fig. B 13-33)

G = mica disks (dia. = I.D., d = thickness in μ or mg/cm²); *L* = solder glass (softening point T_s, expansion coefficient α); *R* = tube (with or without flange) of glass or metal; *P* = data on the sealing process

2. The sealing surface of the metal or glass component must be flat but rough ground.
3. In the case of metals, the sealing surface should be lightly preoxidized by heating in an oxidizing flame to ensure good wetting and vacuum-tight bonding of the solder glass to the metal. To avoid scale formation on the neighboring areas it is recommended that the parts not involved in the joint be previously Ni-plated or Au-plated wherever heating will be applied in the preoxidizing or sealing process.
4. The aqueous, alcohol or xylene suspension, generally applied by camel-hair brush, should not only be painted on to the contact areas of the two components of the seal but also at the edge of the mica disk and usually also over a small annular area on the opposite side, to ensure a reliable sealing of the cut mica edge.
5. The mica disk should be cut quite split-free at the edge (see, e.g., 13.2); the edge should also be superficially cleaned (in case of any finger-prints, etc.) shortly before sealing by wiping with alcohol. The edge should be pressed lightly against the glass-coated sealing face before and during the joining process.
6. A particularly good suspension can be made from lead borate glass (Table T 10–34) which wets mica well and flows at temperatures below the T_{soft} of any ordinary soft-glass component.
7. The sealing process is best carried out in a drop-over electric furnace because of the better temperature control possible. Heating should be carried out for 10 min at 600° maximum (or the mica may split); the joint is annealed at about 400° for $^1/_2$ hr and then slowly (*ca.* 5°/min) cooled to room temperature.

8. Well-made seals can withstand tube degassing temperatures up to 300° without trouble.

Figure B 13-19 shows a series of mica window constructions proved in laboratory and mass-production. Details are given in the legends and the literature quoted.

13.7. Applications of Natural Mica

[13.7] If the advantages and disadvantages offered by mica as a material for HV technology are contrasted, previous discussions readily lead to the following balance-sheet:

A. *Advantages:*

(a) can be punched out to close tolerances;
(b) can be split into very thin flakes with low stopping power for beta and gamma radiation;
(c) low density;
(d) soft; will not scratch glass envelopes;
(e) high elasticity and flexibility;
(f) adequate mechanical strength, even in very thin sheet form;
(g) very low thermal conductivity;
(h) low dielectric losses;
(i) high volumetric resistivity and exceptional electrical breakdown strength;
(j) high degree of vacuum-tightness;
(k) can be joined with the aid of solder glass.

B. *Disadvantages:*

(a) properties vary according to supplier;
(b) compared with glass, is hard to degas;
(c) compared with ceramic, has low maximum operating temperature;
(d) compared with ceramic, has low surface resistivity;
(e) relatively high price, especially for large-area or pure sheet.

The chief uses in vacuum technique are detailed as follows:

(a) *Insulating support and distance pieces* for construction of (mostly upright) electrode systems of tubes up to 50–100 W (especially miniature communication tubes) and of other small tubes, also thyratrons. The thickness of mica for these purposes is 0.2–0.25 mm for small, and 0.3–0.4 mm for larger tubes; the preferred, most practicable sheet sizes are No. 3–No. 6 (Table T 13–1A).

Two mica plates are generally needed as bridges (Fig. B 13-20), held horizontally by the support rods which are sealed into the foot-glass; they form the supports for the individual electrodes. If, in spite of a rough MgO coating on the mica, there is a danger of inadequate insulation because of too many support wires in too close proximity to each other, one may have recourse to the stepwise insulation illustrated in Fig. B 13-21. In this method, the individual metallic components between which especially reliable insulation is required can be attached to different mica disks arranged in stages. In tubes with long cathodes and/or specially sensitive mounts the support frame should be

provided with a wall-stay at least at the end of the mount opposite the foot. The simplest way is to arrange the diameter of the mica disk to be somewhat larger than the I.D. of the glass envelope and to provide the mica edge with serrations (see Fig. B 13-16, specimens *1–3* and *6*) which press elastically against the upper part of the glass and offer an extremely stable support for the mount. For this purpose, the upper part of the envelope is often—especially with large tubes—constricted and domed so that smaller mica diameters can be used and to achieve better conformation with the centering teeth. (See Fig. B 13-22.)

[13.7]

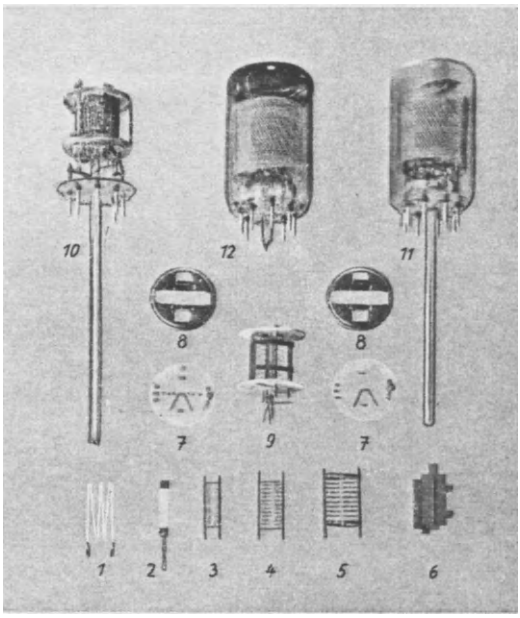


Fig. B 13-20 Components of a small amplifier tube whose mount is held between two mica disks (*7*) (courtesy of SIEMENS, Type C 3 m)

1 filament of alumina-coated W wire (cf. also Fig. B 9.3-12); *2* oxide-coated square cathode sleeve of Ni; *3–5*: 1st–3rd Mo grids; *6* plate of Ni-plated Fe sheet, blackened with a preparation of carbon black; *7* mica support disks; *8* screening plates; *9* assembly of mount on the mica disks; *10* assembly plus screening plates, attached to glass foot; *11* mount with external screening mesh and getter, sealed into glass envelope; *12* pumped and gettered tube

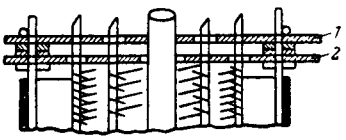
Since toothed mica disks tend to break and exfoliate under vibration (especially in large tubes), manufacturers have recently gone over to support-plates without teeth but with two oppositely-arranged, slight eccentricities, and constrict the I.D. of the envelope by 0.1–0.2 mm relative to the regions of greatest diameter of the mica (see, e.g., RODENHUIS). When the mount is introduced into the envelope, there is only a gentle flexure of the mica disk at the zones of envelope constriction (with no danger of exfoliation of the teeth) and the fit is extremely good, with no play between mica and glass envelope.

In miniature tubes, the method of supporting the mount by current leads sealed into the foot has been mostly abandoned; the whole job of supporting the electrodes is

left to mica disks with toothed edges, one at each end of the mount (see, e.g., Figs. B 5.2-14, No. 2, and B 6.5-2, No. 2). Here too, clearly, the stage system of insulation can be used, as shown by the design of a miniature thyratron in Fig. B 13-23.

The cathode sleeve of I.H. oxide cathodes in such constructions can usually be attached by simple insertion in a mica ring whose size and shape is closely matched to the cathode profile (round, square, oval). Thermal expansion of the Ni sleeve in operation then generally takes care of the problem of tight fit in the support hole of the mica; however, there is in use a series of other constructions, examples of which are shown in Fig. B 13-24. In many cases, it may be an advantage to introduce an

[13.7]



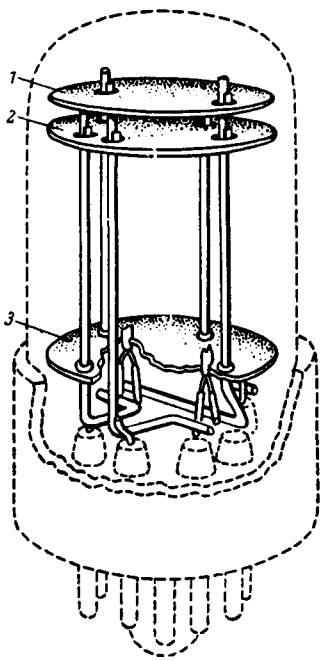


Fig. B 13-21 Attachment of electrode support wires to several superimposed mica disks (staged or tiered insulation)

1 and *2* upper supports consisting of two mica disks; *3* lower mica disk

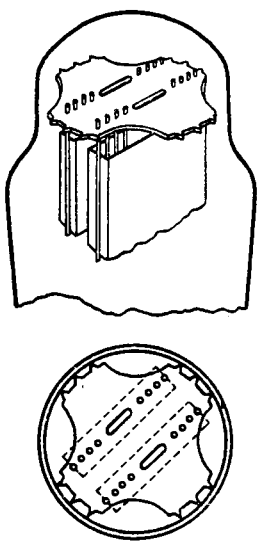


Fig. B 13-22 Supporting an electrode mount and staying it against the envelope wall by toothed, elastic mica disks (cf. also ROBINSON and Fig. B 10-226)

H-or X-shaped hole in the mica at the cathode receiver opening (Fig. B 13-16 specimen 9, and Fig. B 13-25) which creates two elastic tongues to grip the cathode.

In spite of the use of hollow rivets (Fig. B 13-4, II), the electrode support wires are not satisfactorily held. In addition, there is a danger of calcination of the mica disk at the region of contact between it and the hot cathode sleeve; this can cause attrition of the contact zone, especially in long-life tubes, which leads to microphonic noise, and also causes outgassing (cathode poisoning). These two problems of electrode support and

contact attrition has led in many countries to a preference for thin ceramic disks (see 12.5, e.1, especially Fig. B 12-50). To combine the preference for ceramics with the great advantages of mica as a mount support at the glass wall, ceramic bridges have been provided with mica centering flags. The latter are usually small strips with punched slots pushed over projecting lugs on the ceramic bridge normal to the mica surfaces (cf. Fig. B 13-26); the ends of the flags provide an elastic support of the whole mount against the glass wall. For further combinations of ceramic and mica bridges, see 12.5, e.1.

[13.7]

Even if it is decided to make the final tube model with ceramic supports, the use of mica at least during prototype development is cheaper and more convenient, because any holes or slots required in the plate can be made more easily by drilling jigs or simple tools. However, development of ceramics that can be easily machined (Ergan, Porolite, see Chapter 12) has made ceramic a serious competitor to mica even here.

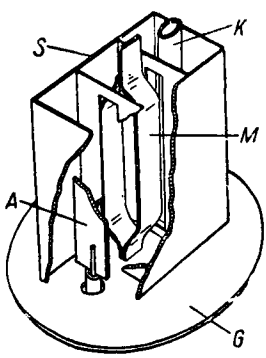
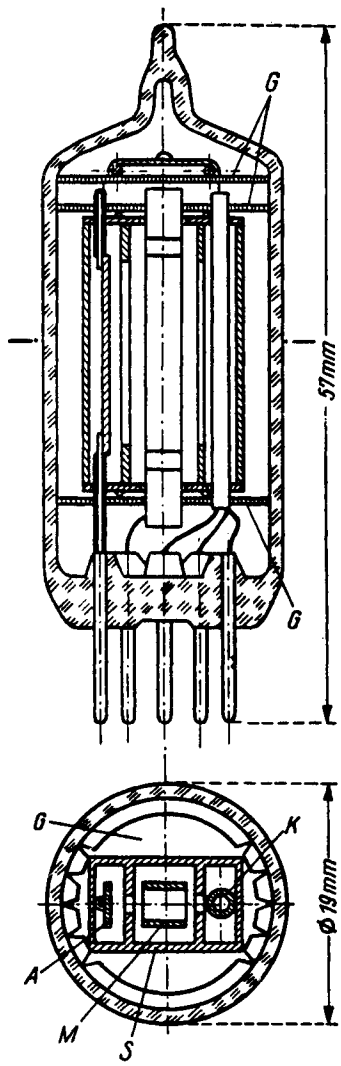


Fig. B 13-23 Design of a xenon-filled miniature thyratron Type 2 D 21 (made by PHILIPS)

K cathode; *M* control grid; *S* screen grid; *A* anode; *G* mica support and stay disk



Mica support bridges near the cathode in amplifier tubes must, just as ceramics, be screened by metal sheet at cathode potential from stray-electron bombardment; if this is not done, the field distribution can be upset.

(b) *Fixing and vibration-damping members* of D.H. oxide cathode filaments (Fig. B 13-27).

[13.7]

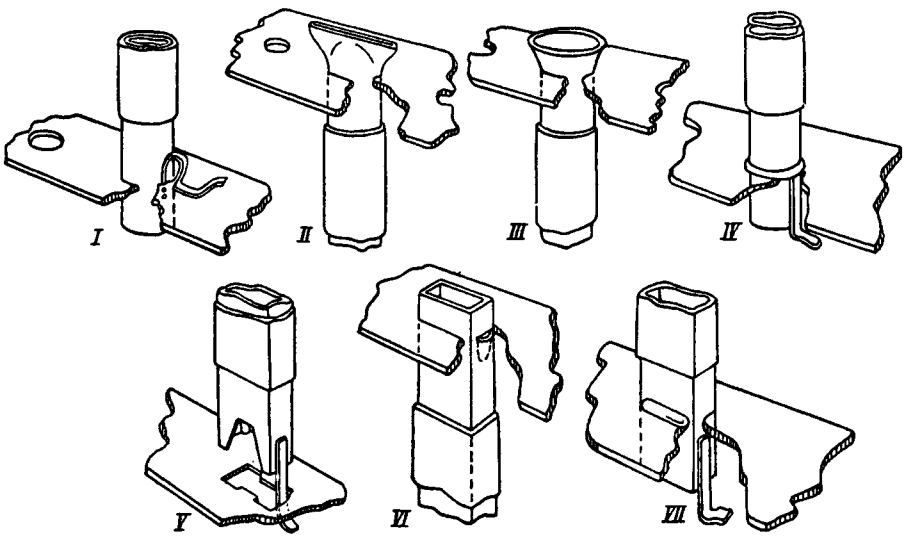


Fig. B 13-24 Examples of methods for holding I.H. oxide cathodes in mica disks (ZAREW)

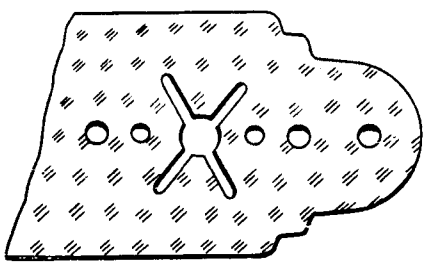


Fig. B 13-25 Punching out leaf-springs in mica disks for supporting cathode sleeves

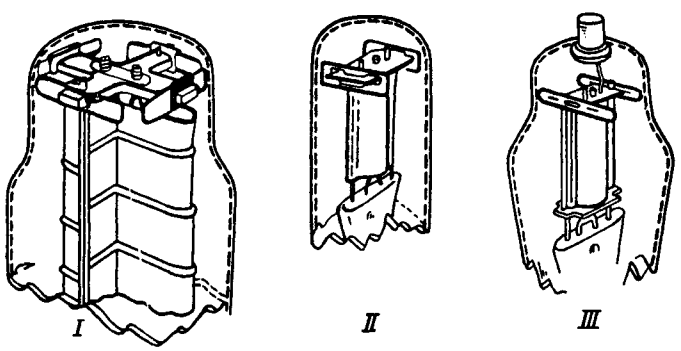


Fig. B 13-26 Supporting and centering methods in small transmitter tubes: ceramic bridges, and slotted mica flags set edgewise on to the bridge to provide elastic support from the glass wall

(c) *Shields to enhance insulation of pinch-foot* and press-foot in photocells (Fig. B 13-28); also for screening the pinch in large gas-filled filament lamps from W deposits and to prevent too much heat transport to the foot by convection of the heated filling gas.

(d) *Elastic sealing (gasket) disks* made of several layers of mica (see Fig. B 8.5-19) between ceramic insulating sleeves for leads and the glass coil sheath of sealed-through

[13.7]

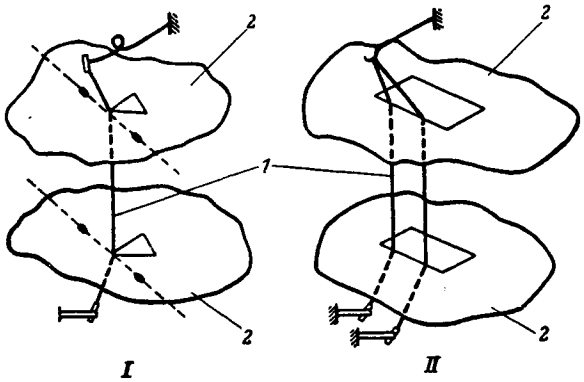


Fig. B 13-27 Fixing methods for D.H. cathode filaments by means of mica disks (ZAREW)
1 filament wires; *2* mica

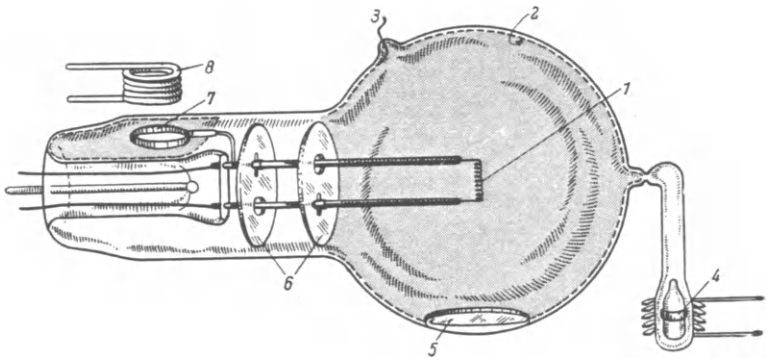


Fig. B 13-28 Screening the pinch and window of photocells with mica disks. The cell is one with a silver substrate evaporated on to the glass wall (LITTMANN)
1 W coil for Ag evaporation, also the anode; *2* cathode mirror on bulb wall; *3* cathode lead; *4* side-arm with Cs-filled capsule and H.F. coil for cracking the capsule open and for introducing Cs vapor to the photocell; *5* mica disk lying loose on the bulb wall to prevent local deposition of Ag and Cs (disk drops to bottom of tube and leaves window clear when tube is raised upright after completion); *6* mica shields to prevent deposition of evaporated Ag and Cs on the pinch; *7* getter support; *8* H.F. coil for flashing getter

current leads; the purpose is to prevent gas discharges and damage to the glass surface from the hard ceramic sleeve.

(e) *Mica cover-plates* to prevent onset of glow discharge on the rear side of the cathode of plate neon lights (surface glow-lamps). However, it should be noted that with glow-tubes (relay tubes) where a high constancy of striking voltage is required,

mica should be avoided if possible, since it increases the cathode fall by slow out-gassing, especially under ion bombardment.

(f) *Insulating interlayers (electrical)* for electrode supports as per Fig. B 13-29.

(g) *Thermally insulating interlayers* between glass walls and nearby metal parts which become hot for short times during H.F. heating. Figure B 13-30 shows a typical case.

(h) *Radiation entry windows* of mica for particle and gamma radiation, in Geiger counters. The thickness in the case of commercial tubes is 2–20 μ (0.7–5.0 mg/cm^2). Thin windows are mainly used for detection of alphas, for X-ray spectroscopy and
[13.7] detection of soft betas such as those from C^{14} or S^{35}. Thicker ones are used for detection of medium-hard and hard betas. See Fig. B 13-13 for the transparency of such mica foils to betas; see Fig. B 13-12A for transparency to soft gammas. For sealing mica windows to make vacuum-tight joints see 13.6, especially Fig. B 13-19; see Fig. B 6.3-7A-

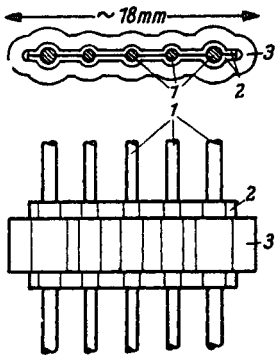


Fig. B 13-29 Supporting and insulating electrode leads by mica (²MO-VALVE)

1 leads; *2* mica interlayers; *3* sheet-copper wrap pressed on

Nos. 2 and 3, and Chapter 17 for cementing with Araldite. Mica windows will support a 1 atm pressure differential (without bracing) when the free diameter is 25–28 mm, and thickness *ca.* 15 μ (G/F = 5 mg/cm^2) according to WU, or 10 μ (3 mg/cm^2) according to BROWN. They flex but remain vacuum-tight. If the thickness is less than 10 μ and the pressure gradient 1 atm, a supporting grid (Fig. B 5.5-12) is recommended; otherwise the pressure difference should be reduced to around $^1/_2$ atm by a gas or vapor filling. In spite of the unavoidable increase in operating voltage and dead time of such "high-pressure" tubes, a suitable filling would be He at 700 Torr plus a little Ar; this still gives a good plateau with tubes whose anode wire is 0.12 mm dia. and working voltage 1500 V, while Ar at such a pressure (+10 Torr of alcohol for quenching) would require too high a working voltage (>2000 V). Obviously, when evacuating and degassing a counter with so thin a window, the pressure gradient must be reduced by having the whole counter in an external auxiliary vacuum which is maintained at the appropriate value for the period of degassing and filling. As an example of the use of very thin and highly-stressed mica window in commercial counters, the Type 410A of the CYCLOTRON-SPECIALTIES, Moraga 8, California (USA) should be mentioned; the window has an unsupported dia. of 62 mm and a G/F of only 0.7–2.3 mg/cm^2. Since the inside of mica windows tend to charge up negatively, which can shift the plateau by as much as 50 V positive and cause hysteresis, it is recommended that the outside be coated with a thin

layer of Aquadag (see 8.5) connected electrically to the cathode. Naturally, this introduces some absorption of the radiation, amounting to about + 0.5 mg/cm² on the window. See, e.g., KMENT for construction and mode of operation of Geiger counters.

Mica-window tubes are mostly made in the form of "bell counters", where the window closes the front end of the cathode cylinder. Figure B 13-31 shows how these are constructed, and Figs. B 13-32 to B 13-32B are photographs of commercial models. As can be seen, damage in transport to the window and also the anode lead is guarded against by suitably-shaped screw-on or push-fit caps. These tubes are also used for measurement of low-energy X-radiation, [13.7] where high absorption in the irradiated gas volume is aimed at (long tube-body); they are also used for beta radiation, where the shortest possible construction is desired to keep the null effect down to a minimum.

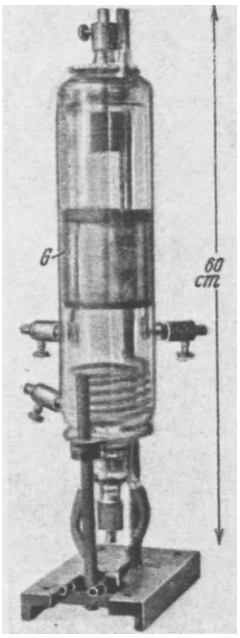


Fig. B 13-30 Wall-current amplifier (Hg vapor tube, see ROTHE, H. and W. KLEEN, *Telefunken-Ztg.* **16** (1935) No 71). *G* = mica lining between amplifier anode and glass wall as heat shield during degassing (LÜBCKE)

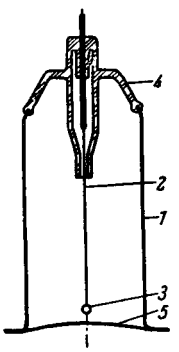


Fig. B 13-31 Schematic illustration of the construction of a bell counting-tube

1 cathode (metal tube); *2* anode (mostly W or Mo wire); *3* glass bead sealed to *2*, to prevent corona discharge; *4* glass foot, support and insulator; *5* mica foil window, sealed or cemented to the flanged cathode tube (see also Fig. B 6.3-7A)

(i) *Power-output windows* (Figs. B 13-19, IV, and B 13-33, sealed to FeNiCr (52/42/6) or CrFe (25/75) or Cu-plated FeNi (50/50)) for throughput of H.F. energy from high-power UHF transmitter tubes of the magnetron and klystron types (COLLINS, DORGELO, MALTER, VARIAN). Because of their thinness (50–200 μ) and low dielectric loss, these windows absorb less power than low-loss glass, whose thickness can hardly be less than 1 mm. In this respect they are inferior only to ceramics (above all pure alumina) which also exceed them in mechanical properties (cf. also Fig. B 12-55). Disk window diameters up to a few centimeters are possible for 50 μ thicknesses of mica. External pressure makes them concave but they do not break.

(k) *Windows for X-ray tubes* ("Ultra soft X-ray tubes", see also BLEEKSMA) of the type shown in Fig. B 5.6-7; they are sealed vacuum-tight in the opening of the anode head and protected from electron bombardment by a Be disk 0.2 mm thick. Diameters are about 15 mm and thicknesses about 20 μ.

[13.7]

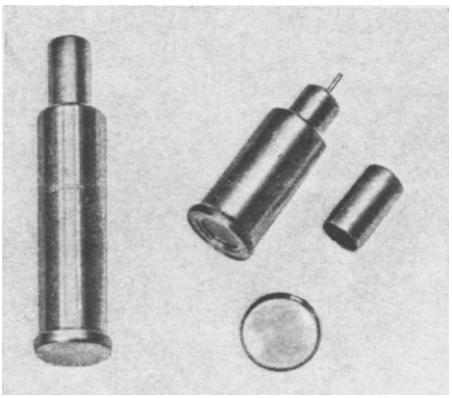


Fig. B 13-32 Counting tubes with mica windows[1] (made by SIEMENS)

Left: interference counter Type IZK-20/75 for crystal structure analysis by X-ray diffraction and fluorescence methods; mica foil: 2 $\pm$ 0.2 mg/cm²; inert gas filling: 200 Torr krypton + 200 Torr argon; counting volume: 20 mm diam., 75 mm effective length; voltage: *ca.* 1700 V; dead time 150 μsec.
Right: bell counter Type GZd-20/25 for measuring very soft betas; mica foil: 1 $\pm$ 0.2 mg/cm²; counting volume: 20 mm dia., 25 mm effective length; voltage: *ca.* 1500 V; dead time: 180 μsec; bell Type GZe-20/25 for very soft beta and alpha radiation; mica foil: 0.7 $\pm$ 0.1 mg/cm²; dead time 250 μsec; other parameters as for GZd-20/25

[1] Constructional details: mica window sealed to Fe flange which is brazed vacuum-tight to the counter body made of Kovar or Vacon (FeNiCo, Table T 6.1-7). The counter body has an inner tube of brass to act as the cathode and is sealed to the Kovar glass foot, through which is sealed the Mo anode wire

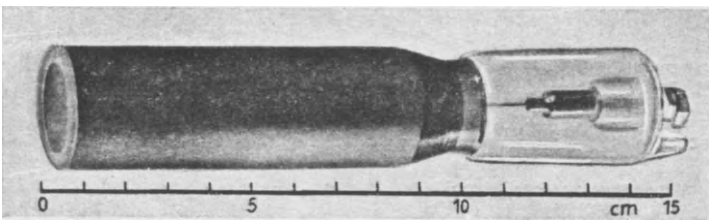


Fig. B 13-32A Geiger counter with mica window, 12 μ thick, sealed vacuum-tight to the cathode cylinder made of CrFe (30/70) (courtesy of PHILIPS) (see also BLEEKSMA)

(l) *Raster plates* of mica 20–50 μ thick:

1. for iconoscopes: These are TV camera tubes with a large mica plate with a mosaic photocathode on one side and a continuous metallic coating on the other (signal plate). The photocathode is an evaporated finely-subdivided Cs-activated Ag layer, each mm² of whose area consists of 10^5 to 10^6 individual photoelements (see Chapter 25). The charge pattern on the mosaic produced by photoeffect from light via optical lenses is scanned by a sharply focused electron beam and discharged, whereby the charge pulses fed to the external circuit by the signal plate modulate the TV transmitter;

2. for super-iconoscopes (intermediate image iconoscopes). Here, the storage mosaic on the mica does not consist as before of many mutually-insulated photocell "islands" but of a thin MgO layer emitting secondary electrons, while on the reverse side of the mica (*ca.* 25 μ thick) a signal plate is applied as before.

The MgO layer is made either by evaporation of Mg in a low pressure of O_2 which puts a MgO "smoke" directly on to the plate, or by evaporation of a metallic layer of Mg on the previously roughened mica and then oxidizing this layer for 10 min at 500°. The picture to be transmitted is then formed—again with an optical lens system—on a homogeneous photocathode which is applied to the inside of the super-iconoscope envelope on one face. The resulting "electron emission picture" of this photocathode is then transferred electron optically to the MgO-coated mica disk at the other end of [13.8]

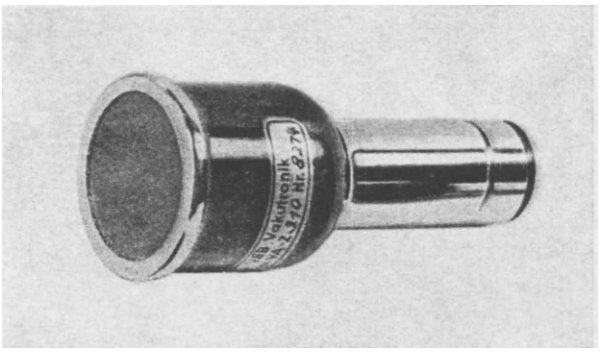


Fig. B 13-32B Geiger counter with glass body, bell construction, with mica window for detection of alpha particles of $E_\alpha > 3$ MeV or betas of $E_{\beta max} > 0.1$ MeV (maker and supplier of photograph: VEB VAKUTRONIK, Dresden)

Cathode: graphite suspension coating on glass tube; gas filling 570 Torr spec-pure He + 7 Torr methylal p.A. ($CH_2(O \cdot CH_3)_2$) as quenching gas. Diameter of clear region of window: 29 mm; overall length of tube: *ca.* 80 mm

the tube and here a charge pattern (picture) is built up again by secondary electron emission; the pattern is scanned by electron beam as in the iconoscope (for details, see, e.g., ECKART, SCHAGEN).

13.8. Synthetic Mica and Substitutes for Mica

The shortage of mica suitable for vacuum work, which arose particularly in wartime, and the variations in properties and impurities associated with a natural material have led in many countries to extensive development work aimed at producing synthetic mica. After the programs undertaken in Germany during the war (see, e.g., LINK, MIDEL, TYLER) were interrupted at the end of the war, an artificial mica was first reported by a small research firm; it was based on fluoro-phlogopite mica $KMg_3AlSi_3O_{10}F_2$ and was made of 30% SiO_2, 35% MgO, 11.5% Al_2O_3 and 23.5% potassium fluorosilicate K_2SiF_6 (ELLEFSON). It is crystalized at atmospheric pressure (INSLEY), and combines most of the main properties of mica. Because of the lack of OH radicals, it contains no

water of crystalization and no water is given off by decomposition on heating. It withstands prolonged heating in dry H_2 at 800° and being an artificial product is free of impurities between layers; such impurities cannot be avoided with natural mica in spite of the most careful choice of pieces.

[13.8]

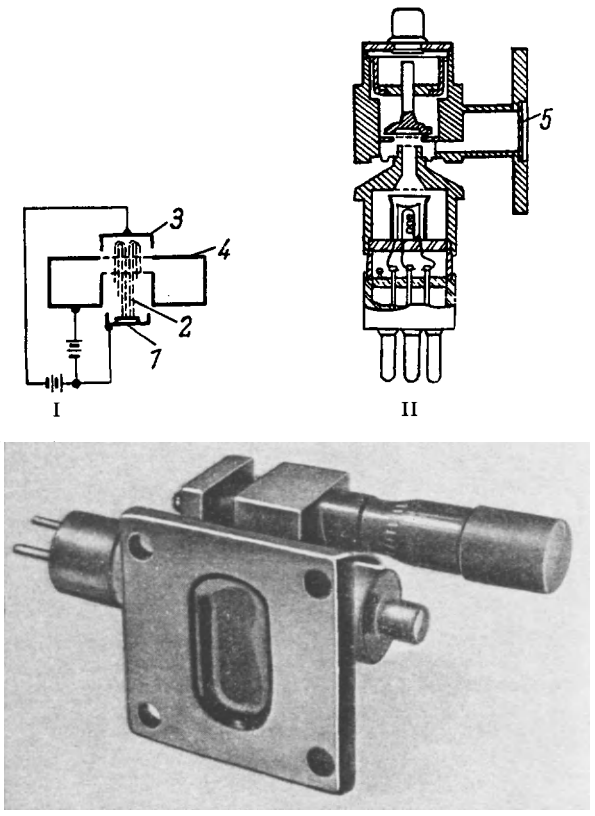


Fig. B 13-33 Variable-frequency (tunable) reflex klystron for 8.2×10^9 to 1.24×10^{10} c/s, power output window of mica 10×23 mm (VARIAN)

I functional design: *1* cathode; *2* electron beam; *3* reflector; *4* resonator; II cross-section: *5* mica window[1] sealed by solder glass; III photograph of tube looking towards window

[1] To fix the FeNiCr frame, with its mica window, to the tube body, the back edge of the frame is mechanically cleaned to remove the oxide layer produced by sealing the window; it is then Ni plated and brazed to the metal body of the USW tube by Ag or AgCu eutectic, in H_2, by H.F. pulse-heating; the mica window must be kept cool during brazing by an internal flow of N_2

Synthetic Ba or B types of mica are similar: compositions are $BaMg_{2.5}AlSi_3O_{10}F_2$ which decomposes at about 900°, and $KMg_3BSi_3O_{10}F_2$, T_{max} *ca.* 750°. Moist atmospheres reduce these temperatures of decomposition somewhat since F is dissolved out in the form of HF. For further details see COMEFORO and LEIZERZON, and Tables T 13–6, T 13–7 based on their data. The GENERAL ELECTRIC also reported some time ago on a new synthetic mica developed by them called "Terratex", with a dielectric constant of

TABLE T 13-6. PROPERTIES OF SYNTHETIC MICAS

		SEE COMEFORO	SEE LEIZERZON			
Composition	–	$KMg_3BSi_3O_{10}F_2$	$KMg_3Si_3AlO_{10}F_2$		$KMg_2LiSi_4O_{10}F_2$	
Density	g/cm³	2.5–3.5	3.1		2.65	
Water absorption	%	0.05–10	1.3		0.40	
Mohs' hardness	–	2–4	–		–	
Max. working temperature	°C	700	1000			
Expansion coeff.	10^{-7}/°C	20–700 °C: 80–130 (see also Table T 13-7)	–		–	
Tensile strength	kg/mm²	Longitudinal: 7				
Compressive strength	kg/mm²	>24.5				
Young's modulus	kg/mm²	At 4.4 kg/mm²: 6060				
TSR (thermal shock resistance)		Low	–		–	
Electrical breakdown strength	kV/mm	8–16				
Electrical breakdown voltage at thickness d	kV		$d=20\mu$ 3.5	$d=50\mu$ 6.5	$d=20\mu$ 10.3	$d=50\mu$ 13.0
Dielectric constant ε (10^6 c/s)		20 °C 5–8	6.7		6.0	
Dielectric loss angle tan δ (10^6 c/s)	10^{-4}	20 °C 3–30	1		1	
Machinability		Very good				

[13.8]

TABLE T 13-7. LINEAR THERMAL EXPANSION COEFFICIENTS OF SYNTHETIC MICAS (COMEFORO)

	α (10^{-7}/°C) IN THE RANGE			
	20–200 °C	20–400 °C	20–600 °C	20–800 °C
$KMg_3BSi_3O_{10}F_2$	89	104	126	146
$KMg_3AlSi_3O_{10}F_2$	92	114	126	135
$BaMg_{2.5}AlSi_3O_{10}F_2$	64.7	77.7	79.0	82.7
Natural muscovite mica(1)	73.7	90.4	92.6	96.3

(1) After pulverizing, formed into a rod.

about 3.5 at 10^7 c/s, dielectric losses as low as natural mica and a lower thermal conductivity (see Fig. B 13-7, curve 3), but GENERAL ELECTRIC has also said that it is still not commercially available (1951) (HAASE). In 1955 a plant was set up by the SYNTHETIC MICA CORP. in Caldwell, N.Y., with an annual capacity of about 1000 tons high-grade mica which would be about 5–10% of the current American requirements. The overall USA requirements up to this time were largely met by imports (mostly from India). NODA has summarized the state of development of synthetic mica in Japan.

A completely different direction of development of a substitute for natural mica is "scale glass"; this can be made from a large number of thin (1–5 μ) scales (flakes) of a SiO_2–B_2O_3–Al_2O_3 glass by heating for 1 hr at 200° under slight pressure (20 kg/cm²); for further details see STEVELS.

For the time being, it would appear that natural mica is still not being replaced in the world's industry (including HV technology) by synthetic mica, mainly because of the very high price of the latter; however, this situation may alter rapidly in the course of further developments and also under pressure from politico-military considerations.

13.9. Molded Mica and Glass-bonded Mica

([1]ANON., BIELER, CROSSLEY, LEIZERZON, MONACK, PFEIFFER, REPLOGLE, RETZOW)

Commercial molded mica ("Micanite") consists of small, shellac-bonded flakes of natural mica and is, therefore, to be used, if at all, in areas where there is no heating or electron bombardment and only in tubes that are continuously pumped. The same applies to glass-bonded mica-powder materials, which have become widely known under the name "Mycalex". Such materials can be made from ground mixtures of lead

[13.9]

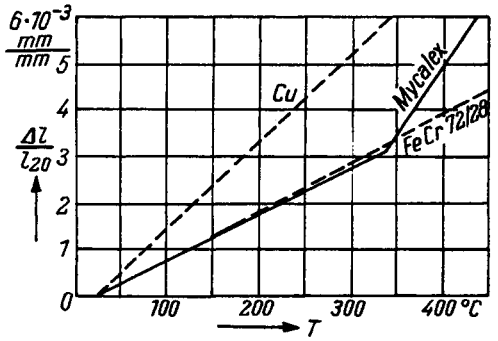


Fig. B 13-34 Thermal expansion characteristic of Mycalex compared with those of ferritic CrFe and Cu (MONACK)

glass B_2O_3, cryolite and mica powder (or synthetic mica powder which permits the use of high-melting hard glasses as binder); these are heated at 620° for $^1/_2$ hr and molded. The binder content is 40–60 w/o. The material is available in the form of sheet (35 × 45 cm², thicknesses of 3–30 mm ± 0.15 mm), round rod (dia. 12–30 mm ± 0.05 mm,

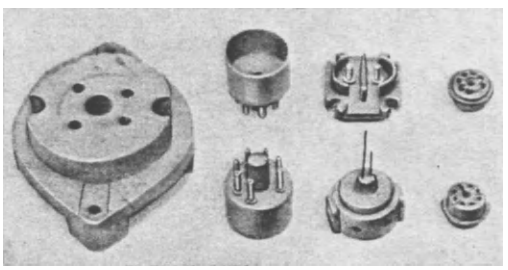


Fig. B 13-35 Tube sockets made of Mycalon (courtesy of the MYCALEX CO.)

up to 50 cm long) and as ready-molded parts (0.2% tolerances) (PFEIFFER). It can be machined with carbide tools (dust-, not chip-cutting), be degassed at 300–400°, and used up to the T_{soft} of the glass binder. Chemically speaking, Mycalex is insensitive to water to the same degree as glass, and to most chemicals, the exception obviously once again being HF. Its chief properties, which clearly vary with the amount and composition of the binder glass, are collected in Table T 13–8. Figure B 13-34 shows a typical expansion characteristic.

TABLE T 13–8. PROPERTIES OF MYCALEX

		FROM PFEIFFER[6]		FROM BIELER	
		SHEET/ PLATE	MOLDED COMPO-NENTS	MOLDED, + 40 % GLASS	INJECTION MOLDED, + 60 % GLASS
Density	g/cm³	2.68	4.4	3.22	3.76
Water take-up	w/o	0	0	0	0
Max. working temperature	°C	–	–	350	350
Max. temp. for continuous use	°C	500	450	–	–
No essential change up to	°C	700	600		
Tensile strength	kg/mm²	4.35	1.5	6.7	3.9
Compressive strength	kg/mm²	27.5	20.5	26	15
Bend strength[3]	kg/mm²	[1] 7.1 [2] 6.8	[1] 7.1 [2] 6.8	12.7	9.8
Impact toughness[4]	kg · cm / cm²	2.6	2.6	–	–
Notch impact strength	kg · cm / cm²	2.0	2.0	–	–
Young's modulus	kg/mm²	–	–	8200	5300
Thermal conductivity	cal / cm s °C	1.8×10^{-3}	2.1×10^{-3}	1.04×10^{-3}	1.07×10^{-3}
Linear thermal expansion coeff. (see also Fig. B 13-34)	10^{-7}/°C	0–100 °C: 98 0–200 °C: 103 0–300 °C: 110 0–500 °C: 128	0–100 °C: 127 0–200 °C: 120 0–300 °C: 113	20–350 °C: 101	20–350 °C: 108
Specific heat	cal/g °C	–	–	0.16	0.13
Electrical resistivity at 17 °C, $F_{rel} = 60\%$[5]	Ω/ square	10^{14}	10^{14}	–	–
Surface resistivity at 17 °C, $F_{rel} = 60\%$[5]	Ω/ square	5×10^{10}	5×10^{12}	–	–
Breakdown strength	kV/mm	22	22	–	–
Dielectric constant ε		10^3 c/s : 7–8	10^3 c/s : 10.5	60 c/s : 7.79 10^7 c/s : 7.68	60 c/s : 9.25 10^7 c/s : 9.10
Loss angle $\tan\delta$	10^{-4}	10^3 c/s : 70 10^6 c/s : 20	– 10^6 c/s : 12.5	60 c/s : 53 10^7 c/s : 13	60 c/s : 70 10^7 c/s : 13

[13.9]

(1) ∥ to molding vector.

(2) Normal to molding vector.

(3) As per DIN 53452.

(4) As per DIN 53453.

(5) Relative humidity of surroundings.

(6) Measured on products of the MYCALEX Co.

TABLE T 13-9. PROPERTIES OF MYCALON WHERE BASICALLY DIFFERENT FROM THOSE OF MYCALEX[1]

Electrical resistivity	Ω-cm	10^{15}
Dielectric constant (10^5–10^8 c/s)	–	9.5
Dielectric loss angle (10^5–10^8 c/s)	10^{-4}	10

[1] Data supplied by the MYCALEX CO. LTD., Cirencester, England.

[13.10] Besides Mycalex, a recent product has appeared for H.F. work; it is called "Mycalon", a glass-bonded, molded mica made by similar methods. Those of its chief properties which differ essentially from Mycalex are given in Table T 13-9. It is used, for example, for tube bases with a high temperature-rating (see Fig. B 13-35).

13. 10. References

AEG: French Pat. 772 300/1933/1934 (Scratch-ruled mica)

ANGERER, E. VON: edited by H. EBERT: *Technische Kunstgriffe*, 9th ed. (Braunschweig, 1954) (p. 108: mica splitting)

[1]ANON.: *AEG-Mitt.* (1928) no. 12 (Mycalex)

[2]ANON.: *J. Inst. Elec. Eng.* **68** (1930) 1313 (Mica)

ANTON, N.: *Ceramic Age* **63** (June 1954) 15–16, 18–19 (Sealing mica windows to CrFe tube with solder glass CORNING 7570)

[1]ASTM Standards, Designation D 351–49 (1949) (Quality classification for mica)

[2]ASTM Standards, Designation D 1082–49 T (Measurement of tan δ and ε)

[3]ASTM Standards, Designation D 652–43 (Measurement of sizes of holes punched in mica using a dial gauge)

BENEDICKS, C.: *Phys. Z.* **32** (1931) 561 (Splitting mica under water)

BIELER, G.: *Silicate Industriels* **15** (1950) 49–50 (Mycalex)

BLEEKSMA, J. *et al.*: *Philips Techn. Rdsch.* **10** (July 1948) 1–13 (Mica windows for ultra soft X-ray tubes and counters for X-ray diffraction equipment)

BOGORODIZKY, N. and M. MALYSCHEW: *Arch. Elektrotechn.* **28** (1934) 644 (Electrical resistance of mica)

BÖHM, H.: *Siemens-Z.* **29** (1955) 324–333 (Transparency of mica to beta rays)

BRIT. ELEC. AND ALLIED INDUSTRIES RES. ASSOC.: Report Ref. D/T 13: The Mechanical Properties of Mica. *World Power* **11** (Jan. 1929) 32–34

BROWN, S. C.: *Nucleonics* (June 1948) pp. 10–22; (Aug. 1948) pp. 50–64; (Oct. 1948) pp. 46–61 (Mica window 10 μ thick, 25 mm dia. for beta counters)

BURMEISTER, H. C.: *Elektrotechnik* **40** (1958) 64–66 (Mica in electrotechnology)

CHOWDHURY, R.: *Handbook of Mica* (Brooklyn, N.Y. 1941)

COLLINS, G. B.: *Microwave Magnetrons* (New York, 1948) p. 684 (Mica plates sealed to metal by glass enamel)

COMEFORO, I. E. *et al.*: *J. Amer. Ceram. Soc.* **36** (1953) 286–294; *J. Amer. Ceram. Soc.* **37** (1954) 427–432 (Properties of types of synthetic mica)

CROSSLEY, P. B.: Brit. Pat. 152 780/1919/1920, DRP 378 522/1919/1923 (Mycalex)

DALE, A. E. and J. E. STANWORTH: *J. Soc. Glass. Techn.* **32** (1948) 147–153 (Solder glass, among other materials, for sealing mica to glass or metal)

DANNAT, C. and S. E. GODALL: *J. Inst. Elec. Eng. (Lond.)* **69** (1931) 490–496 (ε and tan δ of various types of mica)

DONAL, J. S.: *Rev. Sci. Inst.* **13** (1942) 266–269 (Sealing of mica windows to glass tube with solder glass)

DORGELO, E. G.: *Vakuumtechnik* **5** (Dec. 1956) no. 8, pp. 177–189 (Vacuum-tight power-output window of mica for UHF tubes)

EBERT, H.: *Z. Instrkde* **47** (1927) 324; *Phys. Z.* **36** (1935) 258 (Expansion of phlogopite and muscovite mica)

ECKART, F. and C. KUNZE: *Nachrichtentechnik* **4** (1954) 29–33, 81–84 (TV camera tubes)

ELLEFSON, B. S.: *Sylvania Technologist* (1948) no. 4, pp. 7–9, 16 (Synthetic mica)

FISCHER, W. in R. VIEWEG: *Elektrotechnische Isolierstoffe* (Berlin, 1937) pp. 282–284

GRUNDKE, V. and L. ROHDE: *Elektrotechn. Z.* **55** (1934) 1214 (tan δ of glass, quartz, ceramics and mica)
HAASE, A. P. and E. B. FEHR: *Tele-Tech.* (June 1951) p. 30 (Synthetic mica "Terratex" for vacuum tubes)
HALL, E. L.: *J. Res. Nat. Bur. Stds* **35** (1945) 342–353 (Dielectric losses of various types of mica)
HIDNERT, P. and G. DICKSON: *J. Res. Nat. Bur. Stds* **35** (1945) 309–339, 353 (Expansion and tan δ measurements on many types of mica)
HIPPEL, A. R.: *Dielectric Materials and Applications* (New York, 1954)
HOLLAND, D. O. *et al.*: *Proc. IRE* **40** (1952) 587–590 (Gassing of mica due to shock loading which causes friction of metal and glass parts on mica)
HORTON, F. W.: Mica. US Bur. Min. Inform. Circular 6822 (Aug. 1942)
INSLEY, H. *et al.*: *Ceramic Age* (Feb. 1950); *Electronics* (March 1950) p. 120 (Synthetic mica)
KARL, O.: DRP 506 662/1929/1930 (Mica springs for conductor-lead sleeves in gas discharge tubes) **[13.10]**
KEINATH, G.: *A.T.M.: Glimmer als Werkstoff* (Sept. 1932); see also DANNAT (Mica as a material)
KMENT, V. and A. KUHN: *Das GEIGER-MÜLLER-Zählrohr* (Leipzig, 1953) (The Geiger counter)
KRATOCHVÍL, V.: *Výroba elektronek a zářivek* (Czech) (Prague, 1954) (Manufacture of electron tubes and lamps)
LABEYRIE, J.: *J. Phy. et Rad.* **11** (1950) 20; *Le Vide* no. 31 (Jan. 1951) 951–952 (Sealing mica to glass or metal with solder glass enamel/frit)
LANGER, K.: *Feinmechanik. Präzision* **51** (1943) 57 (Use of mica in radio tubes)
LEIZERZON, M. S.: *Radiotechnika i elektronika* **2** (1957) 1077–1081 (Synthetic mica)
LIEBSCHER, F.: *ETZ* (B) **7** (1955) 359–362 (Mica and mica products)
LINDSAY, E. W. and L. I. BERBERICH: *Trans. Amer. Inst. Elec. Eng.* **67** (1948) 734–742 (Breakdown strength of mica at elevated temperatures)
LINK, A. E.: *Synthetic Mica Process* (Ostheim, Germany): CIOS Report File, No. XXII-11 (London, 1945)
LITTMANN, M.: *Getterstoffe u. ihre Anwendung in der Hochvakuumtechnik* (Leipzig, 1938) (Getter materials and applications in HV technology)
LÜBCKE, E. and W. SCHOTTKY: *Wiss. Veröff. Siemens-Konz.* **9** (1930) (1) 390 (Application of mica as a thermal insulator in Hg wall-current amplifiers)
MALTER, L. *et al.*: *RCA Rev.* **7** (1946) 622–633 (Mica windows for power-output windows in USW tubes)
MEUNIER, R. and M. BONPAS: *Le Vide* **8** (1953) 1342–1343 (Sealing thin mica windows to glass tubes for Geiger counters, using solder glass)
MICA FABRICATORS ASSOC.: *Handbook on Fabricated Natural Mica* (New York, 1949)
MIDEL, V. J.: *Report Brit. Elect. and Allied Ind. Assoc.*; Ref. D/T 40 (1948) 14 pp. (Development of synthetic mica during World War II at Siemens)
MINER, D. F.: *Insulation of Electrical Apparatus* (New York, 1941)
MOHR, H.: *Der Nutzglimmer* (Berlin, 1930) (Mica)
MONACK, A. J.: *Ceram. ind.* **48** (1947) nos. 2, 3, 4, 5 (Feb.-May); **49** (1947) no. 1 (July) (Production of Mycalex)
[1]MO-VALVE Co.: *Fabriksvorschrift* (1936) (Degassing mica)
[2]MO-VALVE Co.: Brit. Pat. 378 994/1931/1932; 389 170/1931/1933 (Catkin tubes, use of mica)
NITSCHE, R. and G. PFESTORF: *Prüfung u. Bewertung elektrotechnischer Isolierstoffe* (Berlin, 1940) (Testing and grading insulators)
NODA, T.: *J. Amer. Ceram. Soc.* **38** (1955) 147–152 (Synthetic mica, Japanese research)
PENOTET, H.: *Le Vide* **2** (1947) 260 (Mica in electron tube manufacture)
PFEIFFER und Co.–Hamburg 20: Techn. Information 1957 on Mycalex (Made by MYCALEX Co. LTD, Cirencester, Glos., England)
POPPER, P.: *Nature, Lond.* 4287 (1951) 1419–1420 (UV transparency of mica)
POWELL, R. W. and E. GRIFFITHS: *Proc. Roy. Soc. Lond.* (A) **163** (1937) 189 (Thermal conductivity of mica)
REPLOGLE, D. E.: *Electronic Ind.* **5** (April 1946) 94–96 (Glass-bonded mica)
RETZOW, U.: *Elektrotechn. Z.* **47** (1926) 409, 443 (Mycalex)
RODENHUIS, K. *et al.*: *Philips Techn. Rdsch.* **18** (1956/57) 141–154 (Supporting mica plates by ovality)
ROBINSON, E. Y.: Brit. Pat. 436 606/1934/1935 (Spring disks of mica for constructional supports)
ROHDE, L. and W. SCHLEGELMILCH: *Elektrotechn. Z.* **54** (1933) 581 (tan δ of glass, quartz, ceramics and mica)
ROY, R.: *J. Amer. Ceram. Soc.* **32** (1949) 202–209 (Dehydration of mica)
SCHAGEN, P. *et al.*: *Philips Techn. Rdsch.* **13** (Nov. 1951) no. 5, pp. 123–138 (Mica plates with MgO layer in intermediate image iconoscope)
SCHÖLER, K.: *Feinmechanik. Präzision* **49** (1941) 275–278 (Properties of mica)

SCHRÖDER, R. in H. SCHERING: *Die Isolierstoffe der Elektrotechnik* (Berlin, 1924); *Elektrotechn. Z.* **54** (1933) 541 (Mica)

STEVELS, J. M.: *Philips Res. Rep.* **1** (1946) 129–134 (Scale glass as a mica substitute)

STRONG, J.: *Modern Physical Laboratory Practice* (London, 1944) (p. 388: mica splitting) see also *Rev. Sci. Inst.* **6** (1935) 243

TYLER, P. M.: *Synthetic Mica Research*, FIAT Final Report 746/747 (London, 1947)

VARIAN, R. H.: *Electronics* **25** (April 1952) 112–115 (Mica windows for power output from klystrons)

VERMAN, L. C.: *Standardization* (April 1950) pp. 84–89, 93, 101, 102 (World production of mica, international standardization attempts)

WALSH, E. J.: *Bell Lab. Rec.* (May 1954) pp. 183–187 (Manufacture of miniature tubes)

[13.10] WILLIAMS, A. E.: *The Engineer* (5th March 1948) pp. 227–229 (Mica)

WILSON, E. and H. W. WILSON: *Electrician* **54** (1904) 356, see also *ETZ* **26** (1905) 79–80 (Electrical breakdown strength of mica)

WOOD, W. A.: *Proc. Roy. Soc. Lond.* (A) **163** (1937) 199 (X-ray beam method for expansion measurements on mica)

WU, C. S. *et al.: Rev. Sci. Inst.* **18** (1947) 693–695 (Geiger counter mica windows sealed vacuum-tight with glass powder)

YARWOOD, J.: *High Vacuum Technique*, 2nd and 3rd eds. (1945 and 1948); 4th ed. (1956)

ZAREW, B. M.: *Berechnung u. Konstruktion von Elektronenröhren* (Moscow, 1952); German translation (Berlin, 1955) (Design and construction of electron tubes)

ZEITLER, H.: *Der Glimmer* (Berlin, 1913) (Mica)

ZWETSCH, A.: *Ber. dtsch. keram. Ges.* **32** (1955) 63–69, 236–238 (Thermal expansion of mica)

CHAPTER 14

ASBESTOS

(ČSN-STANDARDS, GRÖBER, NUSSELT, SOMMERFELD, STÄGER, ULLMANN) [14.2]

14.1. General Background, Manufacture, Working

"Asbestos" comprises minerals with an open, flexible fiber structure, which can therefore be spun, woven, or worked up to fiber-board or paper. The materials of prime importance for vacuum work are *serpentine* and *chrysolite* asbestos, found mainly in Siberia (Ural Mts.) and Canada, but also in Cyprus, S. Africa, and Dobšiná (Czechoslovakia). The chief constituents are 43% SiO_2, 44% MgO, 13% H_2O (of crystalization), and often up to 13% iron oxides. For analyses (limiting values) see Table T 14–1.

The raw material is mined, and consists of fine, smooth flexible fibers, fairly strong in tension and easily split, with lengths 2.5 to 100 mm. The color is gray-green to yellow-white with a silky sheen. After cleaning, fibers are generally spun, and cohere better if spun with cotton fibers or talcum (SCHÖLLMANN). Cord and braid can be made from spun fibers. Paper or board can be made from a paste of comminuted fibers, water, and binder (e.g. collodion).

TABLE T 14–1. LIMIT ANALYSIS FIGURES FOR CHRYSOLITE ASBESTOS

CONSTITUENT	w/o
SiO_2	37–44
MgO	39–44
H_2O [1]	12–15
FeO	0–6.0
Fe_2O_3	0.1–5.0
Al_2O_3	0.2–1.5
CaO	Trace–5.0

[1] Water of crystalization.

14.2. Properties of Asbestos

The chief properties of serpentine asbestos are given in Table T 14–2. If heated to 150°, pure asbestos loses its adsorbed H_2O (2–7 w/o). Water of crystalization begins to come off appreciably at 200–300° (Fig. B 14-1, curve 1) from serpentine asbestos, which increasingly loses mechanical strength in the process. At 400–500° (Fig. B 14-1, curve 2) more water of crystalization is released, with gradual formation of anhydrous Mg_2SiO_4. All water of crystalization is driven off at 600°, and for other types of asbestos (e.g. blue hornblende) at 300°. Serpentine asbestos is attacked by HCl, and dissolved by H_2SO_4. Properties of importance in vacuum work are: low thermal conductivity, high electrical resistivity, open structure and therefore low surface conductivity if metal is deposited by evaporation. Obviously, in vacuum, only cotton-*free* material can be used, or outgassing and carbonization during hot-degassing occur. For use in sealed-off tubes, purification is necessary (especially removal of iron oxides), i.e. washing in 10% HCl;

distilled water rinse; drying at 110° (see Table T 14–2 A). This results in loss of strength, however, and short degassing by heating *in vacuo* also weakens the material (Fig. B 14-1, curve 1). Asbestos for furnace use should be free of pyrites (FeS_2; cf. SCHÜR-

[14.3]

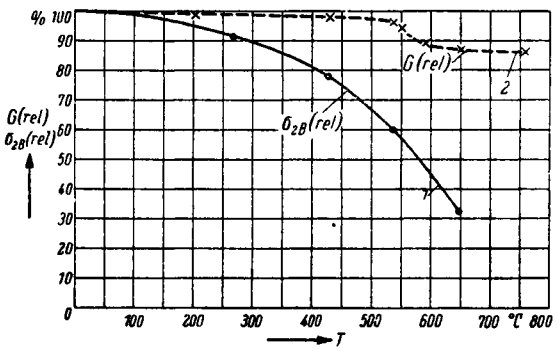


Fig. B 14-1 Relative tensile strength σ_{zB}(rel) of serpentine asbestos after 3 min preheating (curve *1*) and relative weight G_{rel} after 2 hr air-bake (curve *2*): both as functions of preheating temperature *T*

MANN) and $MgCl_2$ (cf. POPP), or the heaters (Ni, CrNi, etc.) will be heavily corroded. In such cases, careful washing in hot distilled water and dilute HCl, followed by rinsing in distilled water are recommended.

14.3. Applications of Asbestos in HV Technology

(a) Seals (coils of asbestos cord) to prevent attack by Hg vapor on soft-solder (Fig. B 9.3-30, No. 7); the large porosity of asbestos permits rapid evacuation of the enclosed sealing space.

(b) Gaskets with Hg overlay (Fig. B 14-2) for continuously-pumped tank rectifiers.

(c) Elastic gasketing of insulation sleeves and electrode leads in gas-filled discharge devices, to prevent initiation of a gas discharge (similar to use of mica, Fig. B 8.5-19, No. 5).

(d) Insulator rings and coatings to prevent formation of conducting layers of evaporated metal condensate on surfaces of glass bridges and pinches (Fig. B 12-55).

(e) Thermal insulation for outer walls of glass envelopes (e.g. to prevent Hg condensation in anode side-arms (Fig. B 12-45, No. 6) or vacuum stills (Figs. B 8.3-1, Nos. 5 and 8, or B 8.4-6).

(f) Internal linings for glass-annealing furnaces (Figs. B 10-171, B 10-172), tube degassing furnaces (e.g. those on automatic pumping equipment with asbestos curtains at entry and exit, Fig. B 10-242), drop-over ovens (Fig. B 10-247, with asbestos-cladding No. 20), Hg stills (Fig. B 8.4-5).

For furnace construction (especially large drying, annealing, and degassing "tunnels" for TV tubes, Fig. B 14-3), a compressed asbestos refractory called

TABLE T 14–2. PROPERTIES OF SERPENTINE OR CHRYSOLITE ASBESTOS

Idealized composition		$(Si_4O_{11})(OH)_6(H_2O)Mg_6$ or $3MgO \cdot 2SiO_2 \cdot 2H_2O$
Density (true)	g/cm³	2.1–2.8 (2.4–2.6)[1]
Mohs' hardness		2.5–4
Melting point	°C	1520–1550[2]
Breaking length		
Pure fiber	km	0.5–1.5, with 6% elongation[3]
8% cotton interweave	km	$\geqq 2.5$
15% cotton interweave	km	$\geqq 5$
Thermal conductivity	cal / cm-sec °C	$(0.2–0.6) \times 10^{-3}$
		200 °C: 40% } more than at room temp.
		600 °C: 60% }
Specific heat	cal / g °C	0.266

[14.3]

[1] Asbestos board, density 1.15 g/cm³ (±10%) with 2.5 w/o moisture (not water of crystalization).

[2] Hornblende asbestos: M.P. 1150°.

[3] For comparison: value for cotton = 18–25 km.
value for natural silk = 25–35 km.

TABLE T 14–2A. CLEANING ASBESTOS FOR USE INSIDE SEALED-OFF VACUUM TUBES

1. Unravel asbestos cord or fibers
2. Boil $^1/_4$ hr in 25% KOH
3. Decant KOH, wash off fibers several times in H_2O, and wring out H_2O left
4. Boil in conc. HCl ($\gamma = 1.19$) for $^1/_2$ hr
5. Decant HCl, wash in H_2O till litmus paper shows rinsing water is acid-free
6. Boil $^1/$ hr in distilled water
7. Decant distilled water, wring out fibers, then slowly air-dry; then dry at 60 °C in oven
8. Cleaned material is very fluffy (voluminous) and has pure white appearance

"Marinite" has recently been marketed: thickness 10–25 mm, panels up to 3×1.2 m², density 0.6 g/cm³ approx. ($\approx$ wood). It is not warped by water, can be worked like wood, and has similar strength. Table T 14–3 gives its chief properties.

(g) Supports for H.F. degassing work-coils (Figs. B 9.2-26, B 9.2-29, or B 9.3-44); insulation for heater leads in furnaces (Fig. B 12-70, No. 8).

(h) Elastic lining between tube-foot and metal of heat-resistant holder (Fig. B 14-4).

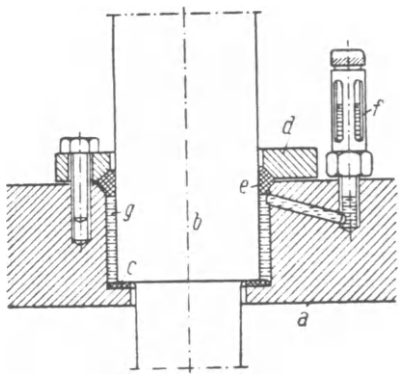
(i) Liner for metal support-clamps of TV envelopes during trolley-pumping (Fig. B 10-250 A).

(k) Thermally-insulating gloves and fingerstalls for operators of glass-working machines.

(l) Powder: filler and insulation in H.F. field-concentrators of sintered carbonyl iron powder (Fig. B 9.2-30).

Fig. B 14-2 Schematic cross-section through a vacuum-tight porcelain-metal joint with asbestos + Hg gasketing (GÜNTHERSCHULZE)

(*a*) Fe envelope-wall of a tank rectifier; (*b*) anode lead-through insulator, porcelain; (*c*) asbestos cord; (*d*) metal flange; (*e*) rubber gasket; (*f*) Hg level-indicator; (*g*) Hg in the joint



[14.3]

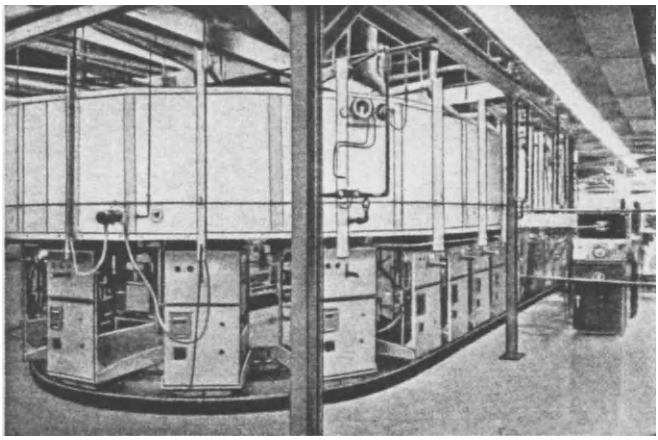


Fig. B 14-3 Large tunnel kiln (for degassing TV tubes) made of three layers of self-supporting Marinite asbestos sheet, each 25 mm thick. Maximum internal temp. 430° (courtesy of FERRANTI LTD., Manchester, England). Cf. also Fig. B 10-250

Fig. B 14-4 Removable tube-holders with asbestos lining for high-temperature rating (cf. also Fig. B 3. 5-8 A)

TABLE T 14–3. PROPERTIES OF MARINITE[1]

MFR.	USA / UK	JOHN MANVILLE, NEW YORK 16 / MARINITE LTD., LONDON, W. 1		
Composition	–	Asbestos fibers + infusorial earth + inorganic binder		
Density, dry	g/cm³	0.54–0.61		
H_2O content, normal	w/o	5		
H_2O absorption	–	Occurs, but not damaged by prolonged immersion in H_2O		
Max. continuous operating temp.	°C	500		
Shrinkage after 50 hr at 500 °C	%	0.6 on length $\leq$ 2.5 on thickness		
Tensile strength	kg/mm²	Dry: 0.7		
Bend strength (20 °C)	kg/mm²	Not pre-fired: 0.63 after 24 hr at 300 °C: 0.5		
Young's modulus, dry	–	(50 kg; 10 mm ball; 10 sec); 1.8		
Max. compressibility	%	At 0.35 kg/mm² load: $\leq$ 2.5%		
Surface hardness	–	Similar to pine wood		
Thermal expansion coeff. (linear)	10^{-7}/°C	20–130 °C: 23; shrinks above 120 °C		
Specific heat	cal / g °C	40 °C 0.23	200 °C 0.28	430 °C 0.34
Thermal conductivity	10^{-3} cal / cm-sec °C	25 °C 0.24	150 °C 0.27	370 °C 0.28

[1] From NORTH THAMES GAS BOARD, Report No. 580/54 D. 044 (Nov. 1955). Data refer mainly to "Marinite 36", density $\approx$ 0.6 g/cm³.

[14.4]

14.4. References

CSN-STANDARDS (Czech) ESČ 126–1949: *Asbest a asbestové výrobky pro elektrotechniku. Vlastnosti a zkoušení* (Asbestos and its products for electrotechnology)

GRÖBER, H.: *Forsch.-Arb. Ing.-Wes.* (1911) no. 104: *Z. VDI* **54** (1910) 1319 (Asbestos)

GÜNTHERSCHULZE, A.: *Handbuch der Physik*, vol. 17: *Elektrische Gleichrichter und Ventile*, 2nd ed. (Berlin, 1929)

NUSSELT, W.: Diss. (München, 1908): *Z. VDI* **52** (1908) 906, 1003 (Asbestos)

POPP, M.: *Kautschuk* **11** (1935) 60 (Asbestos for furnaces)

SCHÖLLMANN, W.: *Das Ganze der Asbestfabrikation*, 3rd ed. (Berlin, 1925)

SCHÜRMANN, E. and W. ESCH: *Kautschuk* **10** (1934) 102, 104, 119 (Asbestos for furnaces)

SOMMERFELD, A.: *Plastische Massen* (Berlin, 1934)

STÄGER, H.: *Elektrotechnische Isoliermaterialien* (Stuttgart, 1931)

ULLMANN, F.: *Enzyklopädie der technischen Chemie*; 3rd ed. (Munich–Berlin, 1956)

TABLE T 10–4 SUPPLEMENT (see pp. 28–31)

American glasses

A 1. Mfr.: CORNING GLASS WORKS

This section of Table T 10–4 contains primarily types of glass usually exported. Some other types and their main properties are collected below.

GLASS NO.	TRADE NAME	α (0—300 °C) [10^{-7}/°C]	STRAIN POINT [°C]	ANN. POINT [°C]	WORK. POINT [°C]
0081	Clear Lime	91 ± 2	483	515	1000
0082	Fluorescent Lime Bulb	88	482	515	
0090	Clear X-Ray Absorb. High Lead	65	448	480	
0100	Clear Non-Lead Low Conductivity	91	502	530	
0110	Iron Sealing	124	428	456	
0121	Soft Television Tube	89	400	432	990
0122	Lead-Free High Exp. Television	88.5	407	439	1015
0280	Hard Lime	83	515	547	
1720	Ignition Tube	42	672	712	1190
1780	Non-Lead Television	91	432	465	995
1781	Non-Lead Dumet Sealing	92	395	424	980
1820	Syn. Bead Glass for Filament Spacer; Clear	98			
1821	dto; Blue	98			
1822	dto; Brown	98			
1823	dto; Green	98			
1824	dto; Pink	98			
2100	Photographic Ruby Bulb	88	425	455	
2471	Photographic Selenium Ruby	92	473	508	
2473	Std. Bulb Ruby	91	471	506	
2540	Heat-Transmitting Red	92	478	510	
3280	Bulb Special Dark Orange	93	476	507	
3320	H. R. Canary	40	497	535	1155
3530	Violet Absorb. Soft Yellow	91	478	510	1090

TABLE T 10–4 *(continued)*

GLASS NO.	TRADE NAME	α (0—300 °C) [10^{-7}/°C]	STRAIN POINT [°C]	ANN. POINT [°C]	WORK. POINT [°C]
3540	Light Amber Lime Bulb	97	473	503	
3550	Dark Amber Lime Bulb	97	480	510	
3718	Light Shade Canary	96	474	507	
4320	New Bulb Green	101	458	486	
5040	Red Purple Ultra; Tubing	92	478	509	965
5380	Blue Lime Bulb A	91	419	450	
5810	Daylight Blue Tank Lime	94	465	496	980
5830	Daylight Blue Lime	98	437	469	990
5890	Visible Absorb. Transmission-A	94	491	523	
5910	Dark Purple U.V. Bulbs	90	491	518	
5911	Extra Dense Vis. Absorb. U.V.	96	486	512	
5970	Red Purple Ultra	112	508	540	
6340	Opal Tubing	80	489	515	
6611	New White	85	438	470	
6992	Photographic Opal	95	469	499	
7030	Heat Resisting	43	519	557	
7051	Sealing Glass	34	505	542	
7120	H. R. Clear Pressware	37	482	515	
7210	U.V. Transmitting Special	35	482	518	
7240	Sealing Glass	21	514	555	
7251	H. R. Clear Electrical	36	489	528	1175
7330	High Pressure Gage	51	527	573	1150
7500	Series Sealing	37	464	498	
7510	Series Sealing	50	479	513	
7530	Series Sealing	71	528	557	
7550	Series Sealing	79	516	546	
7730	Thermo "S"	36.5	507	546	1220
7761	High Stability, Multiform	28	463	507	
7764	Sealing Glass 34	33	445	490	
7981	Spec. Quartz Tungsten Seal	19	640	740	
8110	Fresnel Clear	54	507	541	
8800	Borosilicate (Thermometer glass)	60	530	570	755
9360	Dense Black Tube	87	470	502	
9720	H.T. Ultra Vio.	38	435	475	-
9730	Hard U.V.	42	671	708	
9740	Spec. 185 U.V. Trans.	45	405	450	1250
9820	H. Expans. U.V.T. Special	102	484	515	

TABLE T 10–4. *American glasses* (see p. 35)

A 5. Mfr.: LIBBEY GLASS DIV., OWENS ILLINOIS GLASS CO., *Toledo, Ohio* (USA)

GLASS CODE	GLASS TYPE	α [10^{-7}/°C]	STRAIN POINT [°C]	ANNEALING POINT [°C]	PURPOSE
LA	Lime	99	474	504	
LE-4	Lime	95	487	517	
LE-5	Lime	87	496	527	
LE-8	Lime	101	465	494	
LF	Lime	94	471	502	
LG-12	Lead	87	406	436	For Dumet seals
LG-12-7	Lead	93	463	494	
L-605	Borosilicate	49	475	505	For Kovar and Fernico seals
L-704	Borosilicate	49	449	481	
L-705	Borosilicate	46	468	499	
L-772	Lead Borosilicate	36	485	515	For tungsten seals

For A 6 see p. 651.

A 6. Mfr.: KIMBLE INDUSTRIAL GLASSES, OWENS ILLINOIS GLASS CO.[1]

CODE OR NAME	γ	$\alpha^{(2)}$ (0—300 °C)	$\alpha^{(2)}$ (25 °C—T_{an})	T_{str}	T_{an}	T_{soft}	T_{work}	$\log_{10} \varrho$ [Ω-cm] AT				ε (10^6 c/s)	tan δ (10^6 c/s)	PHOTO-ELECTRIC CONSTANT	REFRACTIVE INDEX
								50 °C	150 °C	250 °C	350 °C				
	[g/cm³]	[10^{-7}/°C]	[10^{-7}/°C]	[°C]	[°C]	[°C]	[°C]						[10^{-4}]	(BREWSTER)	n_D
"Insulator"	2.49	89	106	493	523	715	1020	11.5	8.4	6.5	5.2	7.1	≈ 80	2.5	1.52
K-30	2.67	90	103	410	442	660	1030	17[4]	12.3	9.3	7.3	6.2	15	2.7	1.52
K-52	2.64	89	105	415	447	655	1018	17[4]	11.9	9.0	7.0	6.4	≈ 20	2.6	1.52
K-51	2.54	93	111	454	485	682	999	14.7[4]	10.5	8.0	6.2	6.7	≈ 30	2.5	1.52
K-650	2.25	51	61	472	502	705	1015	13.5	9.9	7.7	6.2	5.1	55	3.7	1.48
K-704	2.24	49	59	449	481	713	1065	16[4]	11.7	9.2	7.4	5.0	≈ 30	3.8	1.48
K-705	2.25	47	56	466	496	709	1011	15[4]	11.1	8.6	6.9	4.8	35	3.8	1.48
K-772	2.35	36	50	486	518	755	1120	16[4]	11.8	9.1	7.4	4.6	≈ 20	3.6	1.48
KG-12	3.05	89	101	400	433	630	980	18[4]	13.0	9.9	7.8	6.7	15	2.9	1.56
N-10	2.54	59	75	528	557	754	1090	11.9	8.7	6.8	5.5	6.4	≈ 110	3.1	1.52
N-51 A	2.36	49	63	542	574	795	1175	12.1	8.9	6.9	5.6	5.6	≈ 110	3.2	1.49
R-5 / R-6	2.53	93	111	493	522	702	984	11.9	8.6	6.6	5.2	7.2	85	2.4	1.52

[1] From W. H. KOHL: *Materials and Techniques for Electron Tubes* (New York, 1960).

[2] Expansion coefficient.

[3] Contraction coefficient.

[4] Extrapolated values.

TABLE T 10-4. *Dutch commercial glasses* (see pp. 64-65) *H I. Mfr.:* PHILIPS

CODE NUMBER	γ [g/cm³]	α (30—300 °C) [10^{-7}/°C]	TEMPERATURE FOR VISCOSITY η = $10^{14.6}$ P (STRAIN P.) [°C]	$10^{13.4}$ P (ANN. P.)]°C[	$10^{7.6}$ P (SOFT. P.) [°C]
01	3.00	92.5	400	425	620
03	2.55	101.5	475	500	680
06	2.55	98.5	480	505	700
08	2.35	39	515	550	770
11	2.55	105	485	505	685
18	2.55	38.5	710	740	955
20	2.55	100.5	495	520	705
28	2.25	48.5	465	495	720
34	2.55	100	480	505	685
39	2.50	99	465	485	665
47	2.60	35	740	770	970
78	3.25	94.5	440	460	645
85	2.65	100	465	495	645
87	2.55	101	490	515	700
112	2.60	35	740	770	970
142	2.20	32	520	555	825
143	2.55	96.5	460	485	685
158	2.25	50.5	490	515	705
162	2.55	95	430	455	670
168	2.55	96	450	475	670

(1) From G. MÖNCH: *Neues und Bewährtes aus der Hochvakuumtechnik* (Halle [Saale] 1959).

GLOEILAMPENFABRIEKEN N. V.[1]

$\log_{10} \varrho$ (Ω-cm) AT		ε AT	$\tan \delta$ AT	NOTES
250 °C	350 °C	1.5×10^6 c/s	1.5×10^6 c/s	
8.8	6.9	7.2	16.2	Bulbs, tubing and rod, for filament lamps and electron tubes
6.6	5.2	7.6	65.6	Bulb glass for filament lamps, flashlight bulbs, and radio tubes
6.1	4.8	7.7	79.3	Glass for X-ray tubes
8.0	6.4	5.2	34.4	Filament lamp bulb, tubing and rod glass; same for discharge lamps, rectifiers (W glass)
6.6	5.2	—	—	Opal glass, bulb glass for filament lamps, tubing for neon lamps
11.5	10	6.3	22.4	Bulb, tubing and rod glass for filament lamps (W glass)
8.5	6.8	—	—	Yellow tube glass for neon lamps
8.8	7.3	5.3	28.5	Bulb and tube glass for X-ray and transmitter tubes (Mo and Fernico glass)
6.5	5.1	7.8	66.5	Tubing for discharge lamps
7.4	5.8	7.1	37.1	UV transmitting (central range) bulb glass for discharge lamps
11.0	9.5	6.4	21.6	Bulb glass for discharge lamps (W glass)
10.3	8.5	8.0	10.7	Tubing for filament lamps, discharge lamps, electron tubes
5.6	4.1	—	—	Red tubing for neon lamps
8.1	6.8	—	—	Tubing for neon lamps
11.0	9.5	—	—	UV-transparent bulb glass for discharge lamps
8.5	7.1	5.0	50.1	Bulb and press glass with high thermal shock resistance
7.9	6.2	7.1	28.9	Tubing and rod for filament lamps
7.6	6.2	—	—	Tubing and bulb glass for X-ray tubes (Mo glass)
8.6	6.9	—	—	Fluorescent-screen and cone glass for TV tubes
8.0	6.3	—	—	Envelope glass for CRO tubes

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